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16. ABSTRACT

This report includes a literature search to determine possible reactions involving sulfur in automotive exhaust systems, an assessment of the effect of various operating parameters (i.e. exhaust oxygen level) on the level of sulfate emissions, and a feasibility study on the use of sorbents as traps to eliminate sulfate from the exhaust gas before release to the atmosphere.

It was discovered in the study that exhaust oxygen level and catalyst age were major variables affecting level of sulfate emissions. Other variables, such as noble metal composition, noble metal loading, catalyst temperature and residence time of the exhaust gas over the catalyst had little or no significant effect on sulfate emissions. It was also discovered that only calcium based materials (such as calcium oxide) removed sulfate efficiently enough with little physical degradation during laboratory testing of potential sorbents. Vehicle tests using the most promising sorbents as traps showed high sulfate removal but with unacceptably high exhaust back pressures.

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I. Summary

The research carried out under this contract assessed the potential for the on-vehicle control of sulfate emissions from oxidation catalyst equipped vehicles. The program was divided into four tasks:

- a literature search on the fate of sulfur in automotive exhaust systems and on possible methods of trapping sulfate in the exhaust system,
- measurement of sulfate emissions from non-catalyst vehicles,
- an assessment of the effect of catalyst and engine operating variables on the level of sulfate emissions, and
- an experimental evaluation of the feasibility of using sorbents to remove sulfate from the exhaust prior to emission to the atmosphere.

In addition, this report contains data on:

- an experimental study of the thermal decomposition of aluminum sulfate which may shed light on the storage and release of sulfate from catalyst surfaces,
- comparisons of different analytical techniques for determining SO_2 and $SO_4^=$ in automotive exhaust, and
- a report by Westvaco Corp. on the potential for using activated charcoal as a reductant for SO_3 in auto exhaust.

Literature Search

The literature search developed data on the thermodynamics of sulfate production, possible reactions of SO_2 and SO_3 in the exhaust system, the oxidation of SO_2 over automotive oxidation catalysts, and the potential for sulfate traps. Thermodynamics indicate that conversions of SO_2 to SO_3 of greater than 50% are possible. At temperatures above 350°C, oxygen partial pressure becomes an important variable in determining the extent of conversion of SO_2 to SO_3. The reaction of SO_2 and SO_3 with both CO and the iron surfaces of the exhaust system are favorable. Also, reaction of SO_3 with the alumina surface of the catalyst is favorable below 425°C.

While the literature on the automotive catalysis of SO_2 is limited, extensive data on the oxidation of SO_2 over Pt catalysts were found. These data indicate that the reaction is first order in SO_2 and that reducing oxygen partial pressure should reduce SO_2 oxidation rate. The functional relationship between oxygen partial pressure and SO_2 oxidation rate is complex.

Calcium oxide appears to be the most promising sorbent for SO_3. Other possible sorbents are oxides of Mg, Mn, and Al.

$SO_4^=$ Emissions from Non-Catalysts Vehicles

As expected $SO_4^=$ emissions from three gasoline powered vehicles (conventional V-8, rotary engine, and CVCC engine) were low, equivalent to less than 1% of the sulfur in the fuel. Conversion of fuel sulfur to sulfate in a diesel vehicle was somewhat higher, averaging nearly 2%. The presence of high amounts of carbonaceous particulate in the diesel exhaust may have caused oxidation of SO_2, either in the sampling or analytical procedure. Further study of $SO_4^=$ emissions from diesels is recommended.

Factors Affecting Sulfate Emissions From Catalyst-Equipped Vehicles

The factors investigated in this task included:

- exhaust O_2 level,
- catalyst age,
- catalyst type (pelleted vs. monolith),
- noble metal composition (Pt vs. Pt-Pd),
- noble metal loading,
- catalyst temperature, and
- residence time of the exhaust gas over the catalyst.

Of these factors, the first two, exhaust O_2 level and catalyst age, were found to have significant effects on sulfate emission rates.

The effect of exhaust O_2 level was studied by comparing sulfate emissions when an air pump was used at all times with sulfate emissions when an air pump was used during cold engine operation only. Lowering exhaust O_2 level in this fashion lowered sulfate by a factor of 5 to 7 on the FTP, and by factors of 2 (for pelleted catalyst) and 10 (for monolithic catalyst) at 96 km/h cruise. Optimization of carburetion should allow these lower sulfate emissions to be obtained without large increases in CO and HC emissions. In-house tests conducted by Exxon Research on the three-way catalyst system, which operates with no excess O_2 in the exhaust, showed sulfate emissions only slightly above those from non-catalyst cars, while CO and HC were controlled to below Clean Air Act Standards. While the three-way catalyst system shows definite promise as a means of simultaneously controlling CO, HC, NO_x, and $SO_4^=$ emissions, further work is necessary to demonstrate the durability of the system.

Tests with catalysts which had been aged for 40 000 km or more on the AMA cycle showed sulfate emissions which were lower than those from fresh catalysts by a factor of 2 or more with no commensurate loss in CO and HC emission control.

Monolithic catalysts emit more sulfate under low speed conditions than do pelleted catalysts, due to the greater sulfate storage capacity of the pelleted catalysts. The sulfate stored by pelleted catalysts under low speed conditions is released during the early stages of high speed operation. After longer periods of high speed operation both types of catalysts emit similar amounts of sulfate.

The other factors examined: noble metal composition (Pt vs. Pt-Pd), noble metal loading, catalyst temperature, and residence time had no significant effect on sulfate emissions, except under conditions where CO and HC control also suffered.

Sulfate Removal From Exhaust Gas By Traps

Four sorbents, 85 CaO/10 SiO_2/5 Na_2O both as pellets and as rings, $CaCO_3$ chips, and ZnO_2 pellets, were tested for $SO_4^=$ removal capability in vehicle tests. The 85 CaO/10 SiO_2/5 Na_2O pellets removed nearly all the $SO_4^=$ in exhaust during a 42 000 km test, but sulfation of the CaO led to unacceptable pressure drop build-up in the trap. Pressure drop increased from an initial value of 1 000 pascals to a final value of 30 000 pascals. Using this sorbent in the form of rings decreased the pressure drop build-up, but also lowered $SO_4^=$ removal efficiency to unacceptable levels. Neither $CaCO_3$ nor ZnO_2 showed good $SO_4^=$ removal efficiency.

A number of potential sorbents were tested under laboratory conditions. Only calcium based materials showed the proper combination of $SO_4^=$ removal efficiency and physical stability.

Tests conducted by Westvaco Corp. indicate that the use of activated charcoal as either a reductant or a sorbent for SO_3 is impractical.

II. Introduction

The purpose of the research carried out under this contract was to assess potential means for on-vehicle control of sulfate emissions from oxidation catalyst-equipped vehicles. These emissions are of concern because of the possible adverse health effects of ambient sulfate. While many questions remain about the effect automotive sulfate emissions will have on ambient sulfate concentrations, and about the levels of ambient sulfate which constitute a health hazard, prudence demands that a thorough investigation of the methods for controlling automotive sulfate emissions be carried out.

All commercial gasolines contain small amounts of sulfur. Recent data assembled by ERDA's Bartlesville Energy Research Center (1) showed a range of gasoline sulfur levels of 0.004 to 0.144 wt. %, with an average sulfur content of 0.033 wt. %. This average was based on nearly 1400 samples obtained nationwide in the summer of 1974. It agrees well with similar surveys conducted in recent years.

In a conventional internal combustion engine, gasoline sulfur is combusted to sulfur dioxide (SO_2), the thermodynamically predicted oxidation product at high temperature. In the absence of an oxidation catalyst emission control system, essentially all of the SO_2 formed in the combustion process is emitted to the atmosphere in that form. Studies conducted by Exxon Research and others (2,3), prior to the beginning of this contract research, indicated that less than 1% of the SO_2 formed in combustion was converted to sulfate in conventional engine, non-catalyst vehicles.

However, when oxidation catalysts are present in the emission control system, some of the SO_2 formed in combustion is further oxidized to sulfur trioxide (SO_3), which can combine with water in the exhaust to form sulfuric acid (H_2SO_4). Sulfuric acid can react with a variety of materials present in the exhaust or the exhaust system to form sulfate salts (MSO_4). Exxon Research's studies indicate that the hydration of SO_3 occurs to completion in the exhaust system, but relatively little further reaction of H_2SO_4 occurs. For the purposes of this report, and to comply with the convention which has developed, SO_3, H_2SO_4, and MSO_4 will be jointly referred to as sulfate.

The fact that some SO_2 is oxidized to SO_3 over noble metal oxidation catalysts used in automotive emission control systems is not surprising. Almost all of these catalysts contain platinum as their major active component. Platinum has been used as a catalyst for the oxidation of SO_2 to SO_3 in sulfuric acid production for many years. While noble metal oxidation catalysts for automotive emission control were under development since the late 1950's, it was not until Spring of 1973 that concern was raised over the potential problems associated with automotive sulfate emissions from oxidation catalyst-equipped cars. The fact that SO_2 emissions from mobile sources contribute less than 1% of the national inventory of SO_2 undoubtedly contributed to this lack of concern

In Spring, 1974, when this contract was initiated, there was general agreement on the following points:

- Sulfate was emitted from non-catalyst, conventional engine vehicles at a level equivalent to less than 1% of the sulfur in the gasoline used by the vehicle.
- Sulfate emissions from oxidation catalyst-equipped vehicles were significantly higher than from non-catalyst vehicles, with conversion of gasoline sulfur to sulfate apparently being a complex function of a number of poorly defined variables.
- Sulfate was stored on oxidation catalyst surfaces under low speed conditions and released under high speed conditions.

There was no general agreement on the amount of sulfate emitted by non-conventional engines, the effect of various catalyst system operating parameters on sulfate emissions, or on the feasibility of using sorbents to trap sulfate emissions in the exhaust system. This program was designed to provide data in most of these areas.

The program was divided into four tasks. Task I involved a literature search on the fate of sulfur in automotive exhaust systems and on possible methods of trapping sulfate in the exhaust system. Results of this literature search were published as an interim report, which has been reproduced, with minor editorial changes, as Appendix A of this report. A summary of the report also appears as Section III of the body of this report.

Task II involved the measurement of sulfate emissions from four non-catalyst vehicles powered by the following engines:

- conventional Otto cycle, V-8 configuration
- rotary
- prechamber stratified charge
- diesel, automotive configuration *

The purpose of this task was primarily to expand the data base from non-catalyst conventional engine vehicles to other non-catalyst vehicles.

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* HDV Diesels were not studied in this program but are being studied under EPA Contract 68-03-2116 with Southwest Research Institute in San Antonio, Texas.

Task III involved an assessment of the factors influencing SO_2 to SO_3 conversion over commercial noble metal oxidation catalysts used for automotive emission control. Factors investigated included:

- catalyst type (pelleted vs. monolith),
- noble metal composition (Pt vs. Pt-Pd),
- noble metal loading,
- catalyst age,
- exhaust O_2 level,
- catalyst temperature, and
- residence time of exhaust gas over the catalyst.

The purpose of this task was to identify those operating parameters of catalytic automotive emission control systems which might be adjusted to minimize sulfate emissions while maintaining CO and HC control.

Task IV involved a study of the feasibility of using sorbents to remove sulfate from the exhaust prior to emission to the atmosphere. Both laboratory screening tests to identify potential sorbents and vehicle mileage accumulation tests to assess sorbent effectiveness were carried out.

III. Task I - Literature Search

Task I involved a literature search on the fate of sulfur in automotive exhaust systems and on possible methods of trapping sulfate on sorbent traps placed downstream of the oxidation catalyst. Results of this literature search were published as an interim report of this program (4). A copy of this interim report, with minor editorial changes, appears as Appendix A of this report. The summary and conclusions of the interim report are repeated below.

Thermodynamics of Sulfate Production

1. At typical oxidation catalyst temperatures, conversions of sulfur dioxide to sulfur trioxide greater than 50% are thermodynamically possible. At lower temperatures even greater conversions are possible.

2. The equilibrium conversion is strongly dependent upon oxygen concentration. At temperatures above 350°C, decreasing the oxygen concentration decreases the equilibrium conversion, suggesting a possible control strategy.

3. Thermodynamics and kinetics show that exhaust sulfur trioxide may hydrate to gaseous sulfuric acid within the vehicle's exhaust system, depending upon driving mode.

4. Thermodynamics show that the gaseous sulfuric acid will begin to condense at about 150°C, which is below the temperature at the tailpipe exit for all driving modes except startup.

Reaction of Sulfur Dioxide and Trioxide with Exhaust Gas Constituents and Exhaust System Components

1. Thermodynamics shows that ammonia will reduce sulfur trioxide to the dioxide. However, exhaust ammonia will be oxidized over the oxidation catalyst before reaction can take place.

2. The formation of ammonium sulfate is favorable only below 225°C.

3. Thermodynamics shows that the reduction of both sulfur oxides by carbon monoxide is favorable.

4. Reaction of both oxides with the iron oxide surfaces of the exhaust system is favorable below 425°C.

5. Reaction of sulfur trioxide with the aluminum oxide catalyst substrate is possible below 425°C. The presence of carbon monoxide may lower this temperature by about 50°C.

Automotive Catalysis of Sulfur Dioxide

1. The rate limiting step in the catalytic oxidation of sulfur dioxide is the surface reaction between adsorbed oxygen and adsorbed sulfur dioxide.

2. The following rate equation appears to represent best the available experimental data for industrial catalysis and should be valid for automotive catalysis;

$$\text{rate} = \frac{k_1 \left(P_{SO_2} P_{O_2}^{1/2} - \frac{P_{SO_3}}{K^e}\right)}{\left(1 + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{SO_3} P_{SO_3}\right)^2}$$

   where k_1 is the rate constant, subscripted P's are the partial pressures of the compounds in the subscripts, K^e is the equilibrium constant of the oxidation reaction, and the subscripted K's are the adsorption equilibrium constants for the compounds in the subscripts.

   This equation is in accord with the above rate limiting mechanism. This equation also indicates a possible control strategy of limiting the amount of oxygen over the catalyst.

3. The automotive catalysis literature is limited. In addition, the data are confounded by many experimental problems, notably the storage/release phenomenon. In general, this literature says that more sulfur trioxide is formed over catalysts than is formed in non-catalyst vehicles.

Sulfate Traps

1. The most promising means of removing sulfur trioxide from the exhaust stream is to react it with a basic metal oxide.

2. Based on a selection criterion consisting of seven requirements, the most promising sorbent material is calcium oxide. Other less promising but still potential sorbents are the oxides of magnesium, manganese, and aluminum.

IV. Task II - Characterization of Sulfur Emissions from Non-Catalyst Vehicles

Task II involved measurement of SO_2, $SO_4^=$, and H_2S emissions from four non-catalyst vehicles: 1) a 1974 350 CID Chevrolet V-8, 2) a 1974 Mazda RX-4 equipped with a rotary engine, 3) a 1974 Honda Civic equipped with a prechamber stratified charge engine, and 4) a 1975 Peugeot 504 GL equipped with a prechamber diesel engine. All four vehicles showed low conversion of fuel sulfur to sulfate and no detectible H2S emissions. In the case of the three gasoline fueled vehicles, sulfate emissions were less than 1% of the sulfur in the fuel. Conversion of fuel sulfur to sulfate was somewhat higher in the diesel vehicle, averaging nearly 2%. The presence of high amounts of carbonaceous particulate in the diesel exhaust may have caused oxidation of SO_2 in either the sampling or analytical procedure, leading to erroneously high $SO_4^=$ values for the diesel. This problem is discussed in greater detail below.

IV.1 Experimental Procedures

IV.1.1 Vehicle Preparation

The four vehicles had previously been used in other experimental programs at Exxon Research. To minimize any effect of these prior test programs on the results of this study, the program called for replacing the exhaust systems on the four vehicles. We were able to do this on all vehicles but the Honda CVCC, which was not commercially available in the U.S. at the time the tests were carried out. Other than changing the exhaust systems and assuring that the cars were in proper mechanical operating condition, no special vehicle preparation steps were taken.

IV.1.2 Test Fuels

Two test gasolines, one containing 0.065 wt. % sulfur, the other containing 0.032 wt. % sulfur, were used in this portion of the program. Both fuels were blended from a base fuel, which contained 0.008 wt. % sulfur, by addition of equal quantities of thiophene and di-t-butyldisulphide. Characteristics of the base gasoline are summarized in Table IV-1.

Table IV-1

Base Gasoline Characteristics

RVP	91.5 kPa (13.3 psi)
% Evap. @ °C	
70°C	33
100	51
150	83
Research Octane	93.0
Motor Octane	82.8
Gravity (g/cc)	0.75
FIA (vol.%)	
Arom	33.9
Olef.	11.5
Sulfur (wt. %)	0.008
Lead (gmn/1)	<0.002

The diesel was also tested on two fuels, one containing 0.17 wt. % sulfur, the other containing 0.35 wt. % sulfur. The lower sulfur level fuel was a standard No. 2 diesel fuel. The higher level fuel was prepared by doping the lower sulfur fuel with an appropriate amount of di-t-butyldisulfide.

IV.1.3 Test Procedure

The vehicles were tested on the high sulfur fuel first. The test sequence consisted of the following parts:

(1) 800 km (500 mile) accumulation - Federal Durability Driving Cycle (AMA Cycle), on an automatic chassis dynamometer.

(2) 1975 FTP,

(3) 20 minute idle,

(4) 2 hrs. 96 km/h (60 mph) cruise,

(5) 1975 FTP (after overnight soak).

The two hour 96 km/h cruise was broken into four half hour periods and separate 20 minute samples taken during each period.

Sulfate emissions were measured by two techniques: Exxon Research's exhaust particulate sampler; and the Goksøyr-Ross technique. Both are described in detail in Appendix B. The Exxon Research exhaust particulate sampler is a CVS compatible, air dilution type sampler which collects particulate, including sulfate, from an isokinetic sample of diluted exhaust. The particulate is collected on 0.2 micron glass fiber filters. Sulfate is leached from the filter with dilute nitric acid, then determined by colorimetric titration with barium perchlorate using Sulfanazo III as an indicator. Details of this procedure are also presented in Appendix B.

The Goksøyr-Ross technique was used on undiluted exhaust and involves condensing and filtering H_2SO_4 at between 60 and 90°C, conditions under which H_2O will not condense out of exhaust. The actual collector used was a modified condenser coil. After completion of a test, H_2SO_4 was washed from the coil and determined using the barium perchlorate-Sulfanazo III method.

SO_2 was also determined by two methods, instrumentally using a TECO UV pulsed fluorescence instrument, and wet-chemically using a hydrogen peroxide bubbler technique. Both approaches are described in Appendix B.

Hydrogen sulfide, H_2S, was determined by the Jacobs-Braverman-Hochheiser technique (5) which is capable of measurement of H_2S at the ppb level. H_2S is absorbed in a bubbler containing cadmium hydroxide solution. This solution is treated with N, N-dimethyl-p-phenylene-diamine in sulfuric acid and ferric chloride to form methylene blue. Methylene blue concentration is then measured spectrophotometrically at 670 mμ.

Gaseous emissions were measured using standard Federal Test Procedure instrumentation, CO by non-dispersive infra-red (NDIR), HC by flame ionization detection (FID), and oxides of nitrogen (NO_x) by chemiluminescence.

IV.2 Results

IV.2.1 Gasoline Fueled Vehicles

As expected, sulfate emissions from the three gasoline fueled vehicles were equivalent to less than 1% of the sulfur consumed with the fuel. The remainder of sulfur in the fuel appeared as SO_2. In all tests, H_2S emissions were below the limit of detection of the Jacobs-Braverman-Hochheiser method, about 0.006 g/km. SO_2 and $SO_4^=$ emissions data for the three gasoline fueled vehicles are summarized in Table IV-2. The 1975 FTP emission results reported in Table IV-2 are the average of the two FTP's run; the 96 km/h results are for the average of the two hour test. Detailed gaseous and sulfur oxide emissions data are presented in Appendix E, Tables E-1 - E-3.

An experimental problem was encountered in testing the Honda CVCC which prevented us from obtaining a full set of data at the 96 km/h cruise condition. The Honda CVCC is a front wheel drive vehicle and cannot be operated normally on the chassis dynamometer. We tested by rotating the car 180° from normal test position and placing the front wheels on the dynamometer rolls. Operation in this fashion was possible only if the dynamometer rolls rotated in the opposite direction from that when a rear wheel drive car is used. With this mode of operation, we were unable to obtain a good match between dynamometer and road load for the Honda. As a result, the vehicle overheated during the 96 km/h, cruise, and it was necessary to test at a lower speed, 80-88 km/hr.

The $SO_4^=$ emission values reported in Table IV-2 were obtained using the exhaust particulate sampler. At these low levels the vehicle $SO_4^=$ emissions caught on the filters approached the blank corrections for the $SO_4^=$ content of the filters themselves, and of the solutions used in their analysis. Thus the absolute emission values in Table IV-2 are less important than the fact that they again verify the conclusion that non-catalyst, gasoline powered vehicles emit little, if any, $SO_4^=$.

TABLE IV-2

SULFUR OXIDE EMISSIONS FROM NON-CATALYST, GASOLINE FUELED VEHICLES

Vehicle	Fuel Sulfur Level, Wt %	Test Mode	SO_2 Emissions		$SO_4^=$ Emissions	
			g/km	% of Fuel S	g/km	% of Fuel S
1974 Chevrolet V-8	0.065	1975 FTP	0.40*	185	0.0005	0.5
		96 km/h	0.15**	124	0.0002	0.6
	0.032	1975 FTP	0.20*	210	0.0005	1.1
		96 km/h	0.075**	123	0.0002	0.9
1974 Mazda RX-4	0.065	1975 FTP	0.50*(0.30)	225(150)	0.0004	0.4
		96 km/h	0.13**	112	0.0000	0
	0.032	1975 FTP	0.65*(0.15)	640(150)	0.0009	2.0
		96 km/h	(0.10)	(135)	0.0002	0.1
1974 Honda CVCC	0.065	1975 FTP	0.20*(0.08)	180(65)	0.0002	0.4
		80-96 km/h	(0.08)	(105)	0.0000	0
	0.032	1975 FTP	0.10*	180	0.0000	0
		88 km/h	(0.04)	(120)	0.0000	0

* Analysis by TECO - Dilute Exhaust
** Analysis by H_2O_2 Bubbler - Undiluted Exhaust
( ) Analysis by H_2O_2 Bubbler - Dilute Exhaust

The SO_2 values in Table IV-2, collected by the TECO instrumental or H_2O_2 bubbler methods, both of which are described in Appendix B, were erratic and invariably high. As discussed in Appendix C, Section C.1.2.1, a number of interferences turned up in using the TECO instrument, including quenching of the SO_2 fluorescence by O_2, CO, and CO_2, and spurious fluorescence by hydrocarbons. Early attempts to correct for these factors were unsuccessful, resulting in the very high SO_2 values, reported in Table IV-2, obtained with the TECO. The most out of line result was obtained with the Mazda, whose rotary engine put out the highest level of hydrocarbon emissions, thereby contributing a large amount of unwanted fluorescence response. The bubbler samples were closer to 100% sulfur balance. However, the three FTP runs monitored by bubbler, from dilute exhaust, ranged from 65 to 150% sulfur balance. As discussed in more detail in Appendix C, Section C.1.2.2, this poor reproducibility and inaccuracy is probably due to the low levels of sulfur dioxide sampled in this test mode. As a result, the sample analyses were not reliable because of the factors discussed in Section C.1.2.2. The cruise samples, on the other hand, gave larger sulfur samples, hence more accurate analyses. They still averaged high, however, about 120%. This is in line with a later study of bubbler accuracy, Section C.1.2.3, which showed this technique to be subject to a bias in this direction for an as yet undetermined reason.

IV.2.2 Diesel Powered Vehicle

Sulfur oxide emissions from the Peugeot Diesel are summarized in Table IV-3. Detailed gaseous and sulfate emissions are reported in Appendix E, Table E-4.

Table IV-3

Sulfur Oxide Emissions From a Diesel Powered Vehicle

Fuel Sulfur Content, Wt. %	Test Mode	SO_2 Emissions* g/km	SO_2 Emissions* % of Fuel S	$SO_4^=$ Emissions g/km	$SO_4^=$ Emissions % of Fuel S
0.17	1975 FTP	0.22	71	0.017	4.2
	96 km/h	0.13	57	0.006	1.6
0.35	1975 FTP	0.29	47	0.012	1.4
	96 km/h	0.24	48	0.010	1.7

* Analysis by H_2O_2 Bubbler - Dilute Exhaust

Sulfate emissions from the Diesel were higher than from the gasoline powered vehicles, as might be expected from the higher sulfur level fuel used. However, measured conversions of fuel sulfur to sulfate were also higher than expected with the Diesel. These conversions averaged roughly 2% for the Diesel as compared with less than 1% for the gasoline powered vehicles. The high level of carbonaceous particulate present in Diesel exhaust, and trapped on the particulate filter, may have promoted oxidation of SO_2 either in the sampling or analytical procedure. Further study of Diesel sulfate emissions, preferably in short term tests in which the build up of carbonaceous material on the filters is minimized, is necessary before firm conclusions can be drawn.

The SO_2 measurements were all low. The reason for this is not known. Possibly the H_2O_2 solutions were not able to completely oxidize the high level of SO_2 entering the bubblers within the available residence time. Another possibility mav be the high level of carbonaceous particulate material which was deposited throughout the collection system. This deposition may also have led to retention of SO_2 by the particulate. As seen in Appendix Table E-4, TECO readings were also low, although this is believed due to particulate fouling of the sample chamber windows.

V. Task III - Factors Affecting Sulfate Emissions From Oxidation Catalyst-Equipped Vehicles

This task involved an assessment of the factors influencing SO_2 to SO_3 conversion over commercial, noble metal, automotive oxidation catalysts. The factors investigated included:

- catalyst type (pelleted vs. monolithic),
- noble metal composition (Pt vs. Pt-Pd),
- noble metal loading,
- catalyst age,
- exhaust O_2 level,
- catalyst temperature, and
- residence time of exhaust gas over the catalyst.

The purpose of this task was to identify those parameters of catalytic automotive emission control systems which might be adjusted to minimize sulfate emissions while maintaining CO and HC control.

V.1 Summary of Results

V.1.1 Exhaust O_2 Level

Of the operating parameters studied, exhaust O_2 level had the greatest effect on sulfate emissions. As part of this program, the effect of limiting exhaust O_2 level was studied by comparing sulfate emissions when an air pump was used at all times, with sulfate emissions when an air pump was used only during cold engine operation, the first two minutes of the FTP. Limiting exhaust O_2 level in this fashion resulted in sulfate emissions which were lower by a factor of 5 to 7 than the full air case, over the FTP. At 96 km/h, elimination of the air pump resulted in sulfate emissions which were lower by a factor of 2 for the pelleted catalyst, and by a factor of more than 10 for the monolithic catalyst. The pelleted catalyst was tested on a car designed to operate lean, without an air pump, and as a result, limiting air pump use had only a small effect on CO and HC emissions. The monolithic catalyst, on the other hand, was tested on a car designed to use an air pump. Limiting air pump use of this car resulted in a relatively large rise in CO emissions, from 2.8 to 5.3 g/km, although HC emissions did not change, showing 0.30 and 0.27 g/km for the two cases. Much of this rise in CO emissions could probably be eliminated by optimization of carburetion.

The ultimate embodiment of the limited exhaust O_2 approach is operation with no excess O_2 in the exhaust, at the stoichiometric point. The exhaust can then be passed over a catalyst, referred to as a "three-way catalyst", which will react the CO, H_2, HC, NO_x, and O_2 in the exhaust to form H_2O, CO_2, and N_2. This approach requires very close control of air-fuel ratio, as close to stoichiometric as possible. If the exhaust is too rich, insufficient O_2 will be available to oxidize

CO and HC, and these emissions will rise. If the exhaust is too lean, NO_x reduction, which does not proceed in the presence of excess O_2, will cease. Since this level of control is beyond the capability of any current open-loop fuel metering system, a closed loop control means is necessary. The most advanced approach for providing such control uses an oxygen sensor in the exhaust to provide feed back control to an electronic fuel injection system.

Tests on a three-way catalyst system were not part of the scope of work of this contract. However, since tests conducted by Exxon Research, as part of its in-house program on control of sulfate emissions, show that sulfate emissions from this system are similar to those from a non-catalyst car, and significantly lower than from a typical oxidation catalyst-equipped vehicle, a discussion of this system has been included in this report.

Tests with a Volvo equipped with a three-way catalyst system consisting of a Bosch oxygen sensor and an Engelhard TWC-9 catalyst showed very low sulfate emissions under all test conditions. For the FTP, this system's sulfate emissions, with gasoline containing 0.03 wt. % sulfur, were 0.0012 g/km. This is only 5% of the sulfate emissions from the monolithic catalyst-air pump case, and very nearly the 0.0006 g/km average usually found for sulfate emissions from a non-catalyst vehicle.

While limited excess air is of definite interest in controlling sulfate emissions, its use may involve some penalties. It is not certain that production vehicles which use oxidation catalysts but not air pumps could generally meet emission standards more stringent than 5.6 g/km CO and 0.56 g/km HC over extended operation. Three-way catalyst systems are still under development. Their durability has not yet been adequately demonstrated. Also, they require replacement of conventional carburetors with electronic fuel injection systems, which raises the price of emission control.

V.1.2 Noble Metal Composition

The data obtained in this program indicated that platinum catalysts might produce more sulfate than platinum-palladium catalysts. This difference, if it does exist, is smaller than the difference found by Beltzer, et al. (6), of Exxon Research, between sulfate emissions for platinum-rhodium and platinum-palladium catalysts.

V.1.3 Catalyst Age

The final factor found to have a significant effect on sulfate emissions was catalyst age. The effect of catalyst age was studied by comparing relatively fresh monolithic and pelleted catalysts with similar catalysts which had been aged 40 000 km or more on the AMA cycle. While the aged catalysts were still adequate for the control of CO and hydrocarbon emissions, their sulfate emissions were lower than those from fresh catalysts by a factor of 50% or more.

The effect of catalyst age on sulfate emissions has been confirmed in a 20 car fleet test underway as part of Exxon Research's in-house program. In this test, 20 1975 California model vehicles equipped with catalysts and, with two exceptions, air pumps, are accumulating mileage over a prescribed road course at an average speed of about 55 km/h. Emission measurements, made every 6 400 km, show relatively low FTP sulfate emissions at 0 km, apparently due to storage of sulfate on the catalysts, peak sulfate emissions, equivalent to about 10% conversion of gasoline sulfur to sulfate, at 6 400 km, and a rapid decline in sulfate emissions thereafter. At 25 600 km most vehicles were emitting about a third of the sulfate emitted at 6 400 km. Detailed results of this test which will continue to 80 000 km will be presented in a Feb. 1976 SAE paper. (7)

These data on aged catalysts are important in two respects. First, the emission factors measured at low mileages may be adjusted for deterioration to reflect the average emissions over the useful life of the catalyst. Second, the fact that sulfate formation activity can be lost without a corresponding loss in CO and hydrocarbon control strongly suggests that it should be possible to design a catalyst which can control CO and hydrocarbon, but would minimize sulfate formation.

V.1.4 Catalyst Type

Monolithic oxidation catalysts emit more sulfate under low speed operating conditions, such as the FTP, than do pelleted catalysts. This is due to the greater sulfate storage capacity of pelleted catalysts. The sulfate stored by pelleted catalysts under low speed operating conditions is released during the early stages of high speed operation. After longer periods of high speed operation, pelleted catalysts emit about the same amount of sulfate as do monoliths. These findings may be useful to the air quality models which would consider actual modes of usage. It was not the purpose of this study to determine which type of catalyst would provide the lower overall level of sulfate emissions in actual use.

V.1.5 Other Factors

The other factors examined: noble metal loading, catalyst temperature, and residence time of exhaust gas over the catalyst had no significant effect on sulfate emissions, except under conditions where CO and HC control also suffered.

V.1.6 Graphic Representation of Results

The information presented above on the effect of catalyst and system operating variables on $SO_4^{=}$ emissions is summarized in Figures V-1 to V-4. Figure V-1 shows $SO_4^{=}$ emissions from pelleted catalysts during the first FTP of the test sequence. Figure V-2 shows average $SO_4^{=}$ emissions from pelleted catalysts for the two hour, 96 km/h cruise. Figure V-3 shows $SO_4^{=}$ emissions from monolithic catalysts during the first FTP, and Figure V-4, average $SO_4^{=}$ for the 96 km/h cruise.

FIGURE V-1

EFFECT OF CATALYST AND SYSTEM OPERATING VARIABLES ON SULFATE EMISSIONS

PELLETED CATALYST — FTP CYCLE

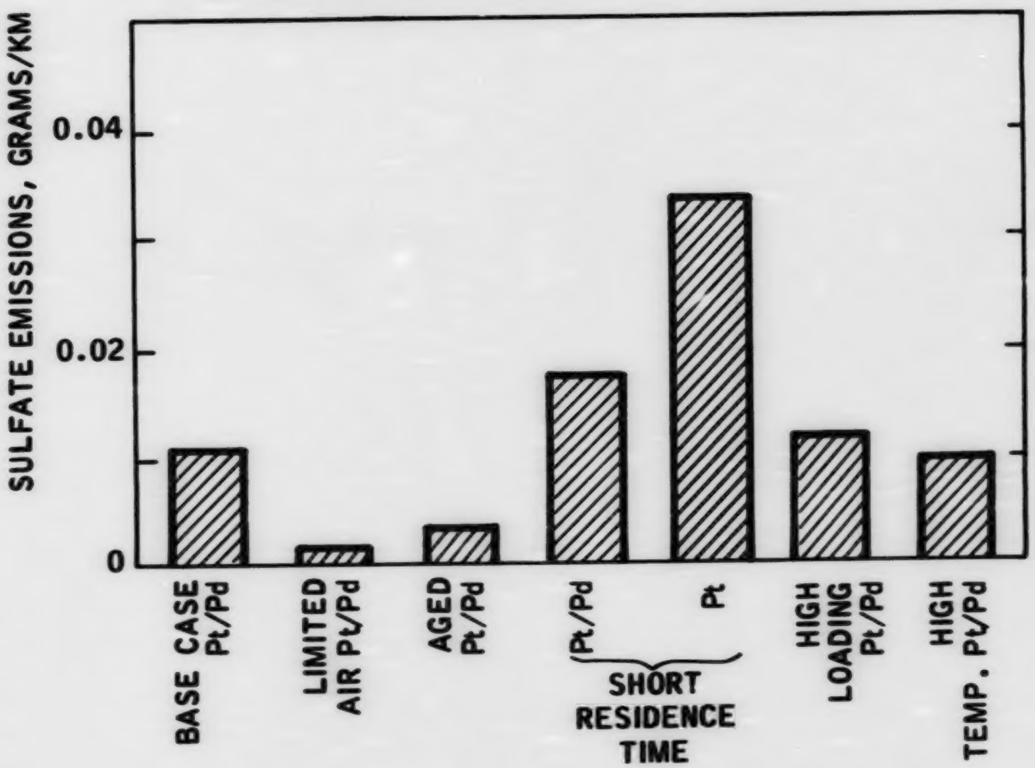


FIGURE V-2

EFFECT OF CATALYST AND SYSTEM OPERATING VARIABLES ON SULFATE EMISSIONS

PELLETED CATALYST—96 KM/H CRUISE

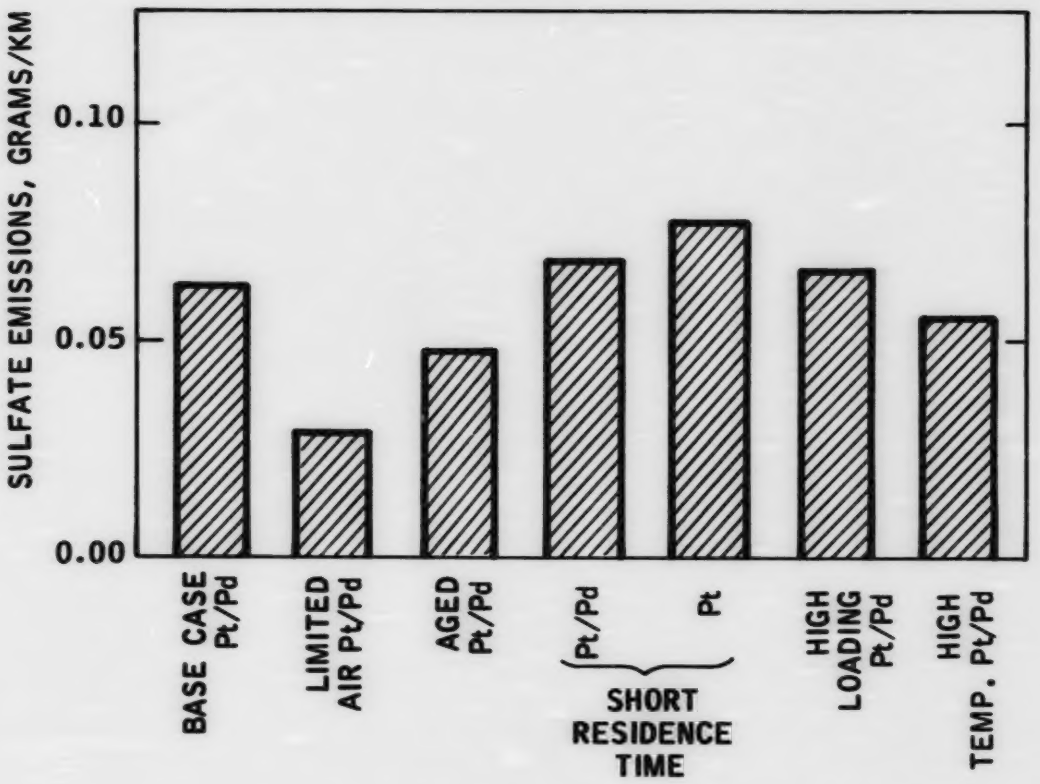


FIGURE V-3

EFFECT OF CATALYST AND SYSTEM OPERATING VARIABLES ON SULFATE EMISSIONS

MONOLITH CATALYST — FTP CYCLE

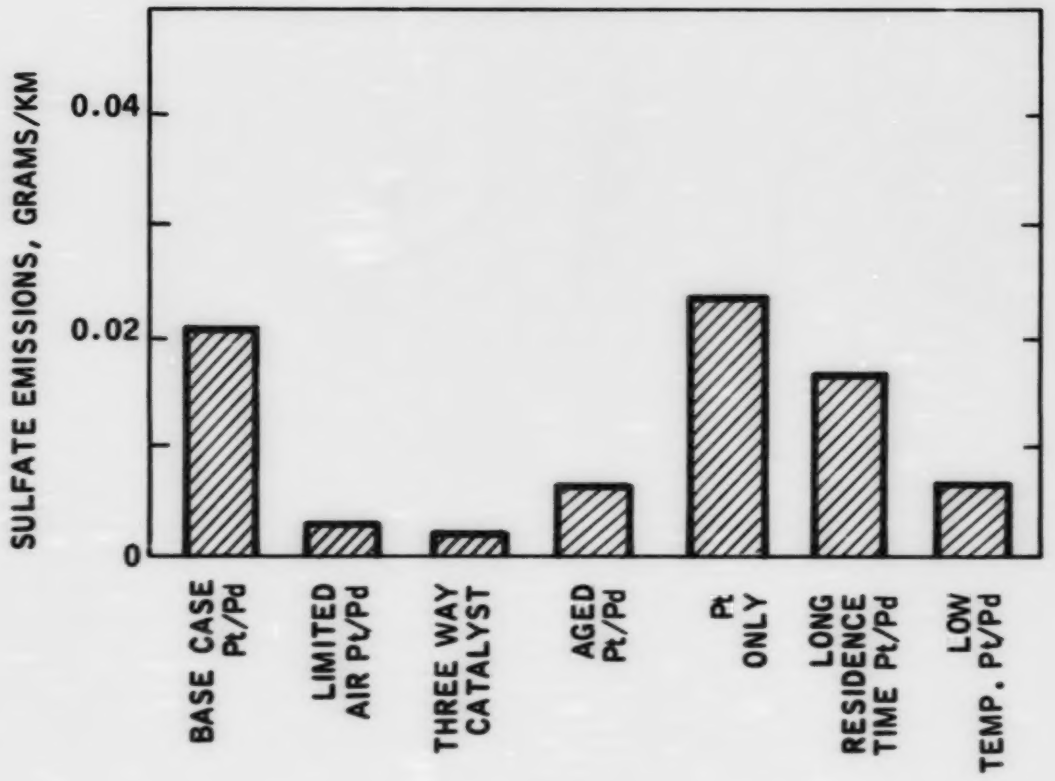
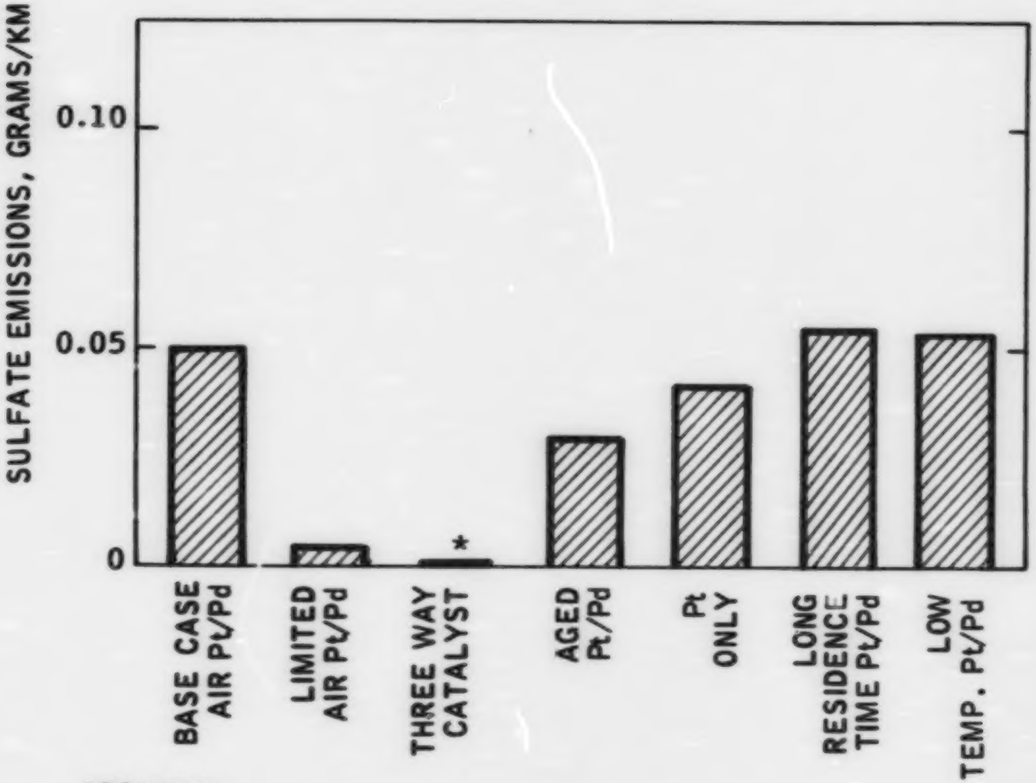


FIGURE V-4

EFFECT OF CATALYST AND SYSTEM OPERATING VARIABLES ON SULFATE EMISSIONS

MONOLITH CATALYST—96 KM/H CRUISE



*88 KM/H

V.1.7 Thermal Decomposition of $Al_2(SO_4)_3$

The thermal decomposition of pure $Al_2(SO_4)_3$ must be understood in order to clarify the role of catalyst sulfur storage in influencing vehicular sulfate emissions. It was studied over a temperature range of 370 to 700°C. This is not a controllable phenomenon, like those just discussed, but it does appear to play an important role in determining the rate of desorption of sulfur oxides by catalysts. Synthetic exhaust gas, containing no sulfur oxides, was flowed over a pelleted sample, and the concentration of SO_2 and sulfate in the exiting gas determined. It was found that the total rate of sulfur oxide release increased with temperature, which was expected. However, the ratio of SO_3 to SO_2 also increased with temperature, which is in the opposite direction from the gas phase thermodynamic equilibrium predictions. Apparently, the decomposition of solid $Al_2(SO_4)_3$ is controlled by the thermodynamics of a different reaction, and the gaseous components were "frozen" in their non-equilibrium ratio by the rapid sampling. In the presence of a noble metal catalyst, such as occurs when $Al_2(SO_4)_3$ decomposes in the vehicle catalyst substrate, the gas phase equilibrium is more rapidly established.

V.2 Experimental Procedures

V.2.1 Vehicle Preparation

Two 2050 kg (4500 lb.) inertia weight, 1975 vehicles meeting the Federal Interim Standards, were used in this study of the feasibility of minimizing $SO_4^=$ emissions through modifications to the catalyst control system. The first was a 5.7 litre (350 CID) V-8 Chevrolet equipped with a pelleted oxidation catalyst. It was modified by the addition of an air pump to reduce its CO and HC emissions to approximately 2.1 g/km (3.4 g/mi.) and 0.26 g/km (0.41 g/mi.) respectively. The second was a 5.7 litre (351 CID) V-8 Ford equipped with air pump and an Engelhard PTX-IIB® monolithic oxidation catalyst which treated half of the exhaust. It was modified by addition of a second monolith on the other side of the engine, lowering CO and HC emissions to about the same level as the first vehicle.

V.2.2 Test Fuels

Two test gasolines were used in this program, one containing 0.032 wt. % sulfur, the other 0.012 wt. %. Both were blended from the base stock described in Table IV-1 and brought up to the proper sulfur level by addition of equal quantities of thiophene and di-t-butyldisulfide. The lower sulfur content fuel was used only in the base case runs reported in Appendix Tables E-5 and E-6. The 0.032 wt. % fuel, representative of the average sulfur content of U.S. gasolines, was used in these and all other subsequent tests.

V.2.3 Test Procedure

Initially, both cars described in Section V.2.1 were broken in for 3 200 km, using a simulated turnpike driving cycle, on our automatic kilometer accumulation dynamometers. The 0.032 wt. % sulfur fuel was used.

After break-in, both cars were tested in a variety of system configurations, to be described subsequently. Initially, the test procedure for each new configuration consisted of preconditioning with the chosen test fuel for 800 km, using either the simulated turnpike cycle or a simulated city cycle. Both driving modes were based on control tapes available at Exxon Research and should not be confused with the LA-4 and HFET driving cycles generated by the EPA. Midway in the program, it was concluded that results obtained with both cycles were sufficiently similar to warrant using only one. It was decided to continue using only the turnpike schedule for preconditioning. By so doing, the number of test sequences for each configuration tested after this decision was cut in half and the preconditioning step was more rapid.

Following the 800 km preconditioning, each vehicle was put through a test sequence as follows:

(1) 1975 FTP
(2) 20 minute idle
(3) 2 hrs. 96 km/h cruise
(4) 1975 FTP (after overnight soak)

The two hour 96 km/h cruise was broken in four half-hour periods, with separate 20 minute samples taken during each period.

Sulfate and SO_2 emissions were measured by the same techniques mentioned in Section IV.1.3 and described in detail in Appendix B; sulfates by the exhaust particulate sampler from dilute exhaust and by the Goksøyr-Ross technique from undiluted exhaust; SO_2 was measured in the dilute exhaust by the TECO instrument and by H_2O_2 bubblers from undiluted exhaust. Gaseous emissions were determined using standard FTP instrumentation; CO by NDIR, HC by FID and NO_x by chemiluminescence.

V.3 Results

V.3.1 Base Case Emissions

The two production vehicles, modified as described in Section V.2.1, were each tested after break-in, under a total of four preconditioning-fuel combinations. The primary aim of these tests was to determine if the target levels of 2.1 g/km CO and 0.25 g/km HC emissions had been achieved, and to provide a baseline of $SO_4^=$ emissions against which the results of future system modifications could be compared.

V.3.1.1 Gaseous Emissions

The four preconditioning-fuel combinations run with these vehicles provide a total of four test sequences, or eight FTP runs, for each vehicle, with which to determine average gaseous emissions. Each car had one FTP run aborted by human error or mechanical failure. The seven remaining FTP runs for each car gave average emission values of 2.3 g/km CO, 0.18 HC and 2.2 NO_x for the pelleted catalyst car, and 2.7 CO, 0.29 HC and 1.9 NO_x for the monolith catalyst car. In all cases these results either satisfied the targets of 2.1 CO, 0.26 HC and 1.9 NO_x, or were deemed close enough to continue the study. The detailed gaseous emission results for these FTP runs, as well as idle and 96 km/h cruise modes are given in Appendix Table E-5 for the pelleted catalyst car and E-6 for the monolith catalyst car.

V.3.1.2 Sulfate Emissions

V.3.1.2.1 Raw Exhaust

Sulfate determinations of the raw exhaust, prior to the catalyst, were made for both cars. This was done, using the Goksøyr-Ross method, to verify the results obtained in Task II, which showed very low sulfate emissions out of the engine. In this case the Goksøyr-Ross readings were taken in one hour segments during the 96 km/h cruise modes, in contrast to the half-hour segments in Task II. This provided larger samples, an aid in achieving accurate analyses. The idle modes were sampled in their entirety, as before. Appendix Tables E-5 and E-6 show these Goksøyr-Ross results. It is seen that the pelleted catalyst vehicle had raw exhaust sulfate levels at or below the values shown in Appendix Table E-1 for a car with a similar engine, at comparable fuel sulfur levels. The monolith equipped vehicle, with a different engine, yielded somewhat higher, although still low, values for engine-out sulfate emissions.

V.3.1.2.2 Post-Catalyst Sulfate Emissions

The most important sulfate results, of course, are tailpipe emissions, after the exhaust has passed over the oxidation catalyst. These are the "filter" values, shown in Appendix Tables E-5 and E-6. During cruises, the 20 minute filter samples were taken, as in Task II, at half-hour intervals. A number of interesting observations can be made. First, the effect of preconditioning mode, turnpike or city driving, appears not to have had a major effect on $SO_4^{=}$ emissions. Thus, comparing average FTP and 96 km/h cruise values for each fuel sulfur level, as shown in Table V-1, no systematic difference is found between the two modes. Primarily because of these results, it was decided to use only one preconditioning mode, and the turnpike cycle was chosen since it allowed more rapid preconditioning. This lack of preconditioning effect is surprising since much work prior to and subsequent to these experiments has clearly shown its importance in determining the storage capacity of the catalyst and hence its $SO_4^{=}$ emission rates. The cycles used here were sufficiently different, 80 and 32 km/h average speeds, to have led one to expect dissimilar effects.

Table V-1

Effect of Preconditioning on $SO_4^=$ Emissions

	$SO_4^=$ Emissions, g/km			
	City		Turnpike	
	0.012 wt. %	0.032 wt. %	0.012 wt. %	0.032 wt. %
	Pellet Catalyst			
FTP*	.003	.006	.002	.007
96 km/h**	.029	.060	.037	.063
	Monolith Catalyst			
FTP*	.007	.026	.007	.023
96 km/h**	.020	.051	.024	.050

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* Average of initial and final FTP
** Average of four half hour tests

Another point worth noting from Appendix Tables E-5 and E-6 is the comparison between the sulfate emissions from initial and final FTP runs of each sequence. In the case of the pelleted catalyst car, three of the four sequences showed higher sulfate values for the initial FTP run. The other sequence showed no change. The monolith catalyst car showed this effect to a lesser extent, and only with the low sulfur fuel, not with the 0.032 wt % fuel.

The explanation for these results seems to stem from the fact that a two hour period of 96 km/h cruise occurred between the initial and final FTP runs of each sequence. During this high speed cruise, as will be shown shortly, it appears that sulfur release from the catalyst takes place. The catalyst was therefore "cleaner" for the final FTP than it was for the initial FTP and tended to retain more sulfur oxides, resulting in lowered tailpipe emissions. This effect is more pronounced for the pelleted catalyst than for the monolith because of the former's greater mass and surface area of alumina. This provides greater storage capacity for sulfur oxides. Storage capacity may also explain why the sulfate emissions during the FTP runs were higher for the monolith than for the pelleted catalyst car. If it is assumed that the relatively low speed FTP driving mode is a "storage" cycle, then the pelleted catalyst should retain more sulfate while the lower capacity monolith allows more to escape.

On the other hand, the 96 km/h cruise sulfate emissions, averaged over the full two hours of each run, were lower for the monolith catalyst than for the pelleted catalyst. This was due primarily to the smaller "spike" obtained during the first half hour of the cruise. Both catalysts tended to give similar results after this period. These results indicate that less sulfur storage occurs during the preceding low speed FTP and idle modes for the monolith catalyst than for the pelleted catalyst, with consequently less release at the beginning of the high speed cruise. Even after reaching a lined out value, the cruise sulfate emissions for both catalysts were higher than during their FTP runs, again indicating that the high speed cruise is not a sulfur storage mode, compared to the FTP driving cycle. The sulfur balance results discussed in the next section will show these effects even more clearly.

V.3.1.2.3 Sulfur Dioxide Emissions - Sulfur Balance

Sulfur dioxide emissions from cars need not be controlled, because of their very small percentage contribution to the total atmospheric sulfur burden coming from all sources, and the fact that this material is only slowly oxidized to $SO_4^=$ in the atmosphere. It is still useful however to monitor SO_2 emissions during $SO_4^=$ testing, even though in the presence of catalysts, a total sulfur balance, comparing SO_2 + $SO_4^=$ emissions with that predicted from the sulfur content and amount of fuel consumed, should not be expected due to storage effects. On the contrary, departures from a 100% sulfur balance indicate whether a catalyst, during a given driving mode, is retaining or releasing sulfur oxides. Therefore SO_2 measurements and their use to calculate total sulfur balances, can help explain sulfate emission results obtained with different catalysts, and driving and preconditioning modes.

Two methods of SO_2 measurement were used. The TECO instrument monitored the SO_2 content of diluted exhaust from the particulate sampler which had been collected in sample bags, while peroxide bubblers were used to directly sample post-catalyst diluted exhaust. These techniques are described in Appendix B and additional tests aimed at comparing the two are detailed in Appendix C. Each has certain advantages and disadvantages. The TECO procedure allows breaking down the two hour cruise period into half hour periods, permitting a more detailed look at the phenomenon of sulfur release from the catalyst. The same could have been accomplished with the bubbler method, but much more chemical analysis time would have been required. On the other hand, the TECO instrument, in reading the contents of the sample bags, during all driving modes, but especially the idle and FTP, was pushed to the limits of its sensitivity. Therefore, the usefulness of its readings is limited primarily to a qualitative evaluation of the change in SO_2 emissions during the half hour periods of the 96 km/h cruise. The bubbler method provided more sample to work with, hence should be more accurate than the TECO method. In particular, the two hour sampling period during the 96 km/h cruise insured a high level of sulfur collection for accurate analysis. Less sample was collected during the FTP and idle periods, with a resultant less accurate value.

A total sulfur balance can be calculated, using the bubbler SO_2 and the filter $SO_4^=$ values, for each driving mode. For the cruises, only an integrated average is shown in Appendix Tables E-5 and E-6, using the two hour bubbler results and the average of the four half-hour filter values. However, the individual half hour TECO values, viewed in conjunction with the half hour filter results, give a qualitative picture of the sulfur balance change during the run. It is seen from Appendix Table E-5 that the FTP values for the pelleted catalyst car were all less than 100%, confirming that this is a sulfur storage mode. The idle modes were also, with one unexplained exception, below 100%. On the other hand, the cruises all averaged over 100%, showing this to be a sulfur desorption mode. To the extent the TECO values are reliable, it appears that SO_2 desorption follows a similar time pattern as does $SO_4^=$, with the highest levels coming off at the beginning of each cruise.

If the monolith indeed shows less storage effect, the differences in sulfur balance between low speed, FTP runs and the high speed cruise should be less pronounced than for the pellet catalyst. As shown in Appendix Table E-6, the sulfur balances for the three test sequences for which complete analyses are available do show a closer approach between FTP and cruise than do the pellet balances of Appendix Table E-5. Thus, the eight FTP runs average a 92% sulfur balance and the three cruises 135%. In contrast, the eight pellet FTP runs average 23% and the four cruises 158%. Finally, the four sets of TECO values show little, if any, change in SO_2 desorption over the duration of the cruises. This behavior is similar to the sulfate emission pattern reported in the previous section for the monoliths.

V.3.2 Effect of Limited Secondary Air

Current vehicle catalyst systems operate with an excess of O_2 over the stoichiometric requirements, to promote oxidation of CO and HC. This additional O_2, supplied by lean carburetion and sometimes augmented by air pump injection into the exhaust gas, also promotes the oxidation of SO_2 to SO_3. In an effort to quantify this effect, and to determine if the level of excess O_2 could be lowered to provide minimum SO_2 reaction while providing satisfactory CO and HC oxidation, a series of vehicle studies have been carried out as part of this contract. These tests were conducted with the base vehicles and catalysts described previously. In both cases, the air pump was operated only during the first 135 seconds of the FTP, to provide more rapid and efficient CO and HC control during this critical portion of the test. Secondary air from the air pump was vented to the atmosphere during the remainder of the FTP and during the idle and 96 km/h modes. In one additional test, a three-way catalyst system with feedback oxygen sensor was also run.

As described in the following sections, these low excess air systems produced dramatic reductions in the level of sulfate emissions. At the same time, control of CO and HC emissions was affected to a much lesser extent. For example, the pelleted catalyst car showed, for the initial FTP runs, a five-fold reduction in sulfate compared to the base case, and only a slight increase in CO. The monolith car showed a doubling of CO, but an eight-fold drop in sulfate emissions. Finally, a three-way catalyst car gave very low CO and HC emissions over the FTP, and sulfate emissions of the same order as for non-catalyst cars.

V.3.2.1 Pelleted Catalyst Vehicle

The amount by which excess O_2 levels were lowered was measured during idle and 96 km/h cruise modes. At idle, it dropped from a range of 5.5-7.7% to about 1-3%. At 96 km/h cruise, the changes were more dramatic; from 3-3.5% to about 0.9%.

V.3.2.1.1 Gaseous Emissions

Beginning with this phase of the program, it was decided to use only the 0.032 wt. % sulfur content fuel, since this most closely represented the national average. Appendix Table E-7 presents the gaseous and sulfate emissions for both turnpike and city cycle preconditioning modes. The two test sequences give an average FTP CO value of 3.38 g/km, HC of 0.20 g/km, and NO_x of 1.96 g/km. These show a slight rise in CO compared to the base pellet catalyst case, Section V.3.1.1.1, but no significant change in HC or NO_x emissions. The CO increase, in part at least, may have been due to an enrichment of the carburetor calibration during the city preconditioned test sequence. The first half hour of the cruise gave CO levels typical of those from the previous cruise; the last 1.5 hours were much higher and the subsequent FTP run yielded the highest CO values of the four FTP runs.

V.3.2.1.2 Sulfate Emissions

The Goksøyr-Ross samples taken before the catalyst were typically low, and not significantly different than for the base case car. Filter samples after the catalyst are much lower than the base case results, however. The two initial FTP runs averaged only 0.002 g/km and the two final FTP runs 0.001 g/km. In contrast, the base case FTP emissions with 0.032 wt. % sulfur fuel shown in Appendix Table E-5 averaged 0.010 g/km for the two initial FTP runs and 0.002 for the final two.

The cruise sulfate emissions were also much lower for the limited secondary air case. The turnpike preconditioned cruise showed the same initial spike in sulfate emissions, followed by a gradual decline, but the absolute levels were about half those found for the base case. The other cruise, following city preconditioning, presented something of an anomaly. A spike was observed for the first half hour, although somewhat lower than for the first cruise. After this, however, sulfate emissions fell rapidly to very low levels. It is believed this is related to the increase in CO emissions due to accidental carburetor enrichment, discussed in the previous section. This is a very dramatic example of the effect of air-fuel ratio on sulfate emissions in the absence of secondary air. Even ignoring the carburetor drift, and looking only at the more consistent sequence, it is clear that removing secondary air after the warm-up phase of the FTP significantly lowered sulfate emissions, as did complete removal of secondary air during the 96 km/h cruise.

V.3.2.1.3 Sulfur Dioxide Emissions

Emissions of SO_2 during the initial FTP of each test sequence, Appendix Table E-7, were higher than those from the final FTP. This meant, of course, that total sulfur balances were higher also. This contrasts with the base case pellet vehicle, where initial and final FTP SO_2 emissions and total sulfur balances were generally similar for both FTP runs of the same test sequence. In addition, the SO_2 emissions and total sulfur balances of the initial FTP runs were much higher for the limited secondary air case than for the base case. This indicates that, when less oxygen is present, the pellet catalyst has less tendency to store sulfur even during the low speed FTP mode, and under certain conditions, it may actually release a small amount of previously stored sulfur.

The 96 km/h cruise results show that the tendency to release sulfur in the absence of secondary air is accentuated at high speeds. The consistent sequence showed a sulfur balance of 199%, showing the by now usual initial spike. When the carburetion began to richen out, this rose to 267%, and the spike effect was washed out by the change in air-fuel ratio. Both values are higher than those observed for the base case at the same fuel sulfur content. This "cleaning" process was apparently so effective that the final FTP runs, following the cruise modes, were now capable of again storing sulfur, even with limited secondary air. It would seem then that the sulfur content of the catalyst, when sulfur sorption or release occurs, is a function of the level of oxygen in the exhaust gas.

V.3.2.2 Monolith Catalyst Vehicle

The limited secondary air procedure was tested on this vehicle using only the turnpike preconditioning mode, with the 0.032 wt. % sulfur content fuel. Gaseous, sulfate and SO_2 emissions are given in Appendix Table E-8. Excess O_2 levels, which had been about 7% at idle and 4-4.5% at 96 km/h cruise, when the air pump had been used, fell to around 2 and 0.7% at idle and cruise respectively when the pump was vented.

V.3.2.2.1 Gaseous Emissions

The FTP CO emissions rose more with limited secondary air, compared to the base case, than occurred with the pellet catalyst vehicle. Thus the average CO value for the limited secondary air monolith catalyst car was 5.3 g/km, compared to only 2.7 g/km for the base case monolith catalyst car. Average HC and NO_x emissions did not change, however, from the base case.

The increase in CO emissions may be due to the fact that the car used for the monolith catalyst studies was originally equipped with an air pump, and its carburetion may have accordingly been set relatively rich. The car equipped with the pellet catalyst was designed for use without an air pump and may have had a leaner carburetor calibration to compensate. Unfortunately, no measurements are available of average air-fuel ratios over the FTP.

V.3.2.2.2 Sulfate Emissions

Sulfate emissions from this car were much lower than from the same vehicle using an air pump full-time. The two FTP runs gave identical sulfate values, 0.003 g/km, compared to an average of 0.023 at the same fuel sulfur level for the full air case. Cruise results were only between 0.003 and 0.005 g/km, compared to an average 0.050 for the full air case. No pattern was observed for the four separate half-hour cruise samples. These results are in agreement with those obtained on the pellet catalyst car, showing that limiting excess air has a significant effect in reducing sulfate emissions from catalyst-equipped cars.

The Goksøyr-Ross pre-catalyst samples showed unusually high levels of sulfate emissions in the raw exhaust, about equivalent during cruise, to the post-catalyst filter samples. The reason for this is not clear. Some type of experimental problem is the most plausible explanation at this time.

V.3.2.2.3 Sulfur Dioxide Emissions

Emissions of SO_2 during the cruise were, as indicated by the TECO values, constant. The more quantitative H_2O_2 bubbler results yield, together with the average of the four filter sulfate values, a sulfur balance of about 120%. The two FTP runs show a puzzling difference, with the first showing a sulfur balance of 32% and the last, 109%. In the full air pump case with this car, Appendix Table E-6, sulfur balances were similar for initial and final FTP runs. No explanation is available for this finding, and insufficient data exist to confirm its reality.

V.3.2.3 Three-Way Catalyst Results

Since limited excess O_2 in the exhaust has been found to be effective in minimizing $SO_4^=$ emissions, a logical extension of this approach is operation with no excess O_2, at the stoichiometric point. The exhaust can then be passed over a catalyst, referred to as a "three-way catalyst" (TWC) which is designed to react the CO, H_2, NO_x and O_2 in the exhaust to form H_2O, CO_2, and N_2.

This approach, which is still in an early stage of development, requires very close control of air-fuel ratio, as close to stoichiometric as possible. If the exhaust is too rich, insufficient O_2 will be available to oxidize CO and HC, and these emissions will rise. If the exhaust is too lean, NO_x reduction, which does not proceed in the presence of excess O_2, will cease. Since this level of control is beyond the capability of any production open-loop fuel metering system, a closed-loop control means is necessary. The most advanced concept for providing closed-loop control uses an O_2 sensor in the exhaust.

To determine whether closed-loop control of exhaust O_2 content would provide the desired reduction in $SO_4^=$ emissions, a Volvo equipped with a feedback control system using a Bosch O_2 sensor and a three-way catalyst developed by Engelhard was tested. All tests were run with fuel containing about 0.03 wt. % sulfur.

This car was tested after the system had accumulated 6 400 and 25 000 km of aging. An FTP at the lower kilometer level gave results of 1.04 g/km CO, 0.14 HC, and 0.56 NO_x. Sulfate emissions were only 0.8 mg/km. At the higher kilometer level, a similar FTP showed 2.12 g/km CO, 0.23 HC, 0.46 NO_x, and 1.7 mg/km sulfate. An EPA Highway fuel economy test at 25 000 km was also run, yielding only 0.4 mg/km of sulfate emissions.

These few tests indicate the potential of the three-way catalyst system to simultaneously control gaseous emissions while producing only very low amounts of sulfate. Much more work is needed, however, to demonstrate the durability and practicality of this system for large scale use.

V.3.3 Effect of Residence Time

The effect of residence time, defined here in terms of space velocity, was also investigated on vehicles using both pelleted and monolithic Pt-Pd catalysts. For the pelleted catalyst, high space velocity was created by replacing the standard 4.25 litre converter with a smaller 2.6 litre unit. The smaller converter normally contains higher noble metal concentration catalyst. For these tests, it was filled with the lower noble metal concentration catalyst normally used in the larger converter. For the monolithic catalyst, lower space velocity was created by placing two monoliths in series on each side of the engine.

V.3.3.1 Pelleted Catalyst Vehicle

V.3.3.1.1 Gaseous Emissions

The results for this test sequence, conducted with the 0.032 wt. % sulfur fuel and turnpike preconditioning, are shown in Appendix Table E-9 and can be compared with those shown for the same vehicle, but using a full size 4.25 litre catalyst converter, in Appendix Table E-5.

Average FTP values for the small converter, high space velocity vehicle are 2.0 g/km for CO and 0.16 for HC. These compare closely with the average values of 2.3 and 0.18 obtained with the conventional car, indicating little, if any, effect of space velocity, over the range investigated here, on FTP gaseous emissions of CO and HC. At higher overall flow rates, 96 km/h cruise, where a greater space velocity effect on oxidation efficiency would be expected, there is a very slight increase in CO but essentially no effect on HC. Thus, the CO emissions with the smaller converter at cruise mode average 0.07 g/km, compared to 0.03 g/km for the larger converter. Hydrocarbon emissions averaged 0.02 g/km for both configurations.

V.3.3.1.2 Sulfate Emissions

Surprisingly, the initial and final FTP sulfate values were higher than those measured for the base case with the same fuel. The base car averaged 0.010 g/km for the two initial FTP runs made with 0.032 wt. % sulfur fuel, but the smaller converter gave a value of 0.018 g/km sulfate. Similarly, the two final FTP runs on the base car yielded an average of 0.002 g/km sulfate, compared to 0.008 for this configuration. Efficiency of SO_2 oxidation to sulfate would be expected to decrease, or stay the same with increasing space velocity. The reason for this anomalous finding, or whether it is real, is not known. Perhaps the rate of removal of sulfate from the exhaust gas via reaction with the catalyst wash coat is affected more by residence time than is the oxidation of SO_2 to SO_3. This would explain the escape of more sulfate at the shorter residence time.

During the 96 km/h cruise, the typical initial spike of sulfate was observed, and the two hour average was 0.068 g/km, comparable to the 0.062 found for the base car.

V.3.3.1.3 Sulfur Dioxide Emissions

The bubbler values show, for the initial and final FTP runs, a drop in SO_2 emissions, leading to a fall-off in total sulfur balance from 33% for the initial FTP to 15% for the final. This pattern differs from the base configuration, where first and last FTP run sulfur balances were similar. During the cruises, the combined bubbler value and the average of the four filter samples shows a total average sulfur balance of 158%, comparable to that found with the base car.

V.3.3.2 Monolith Catalyst Vehicle

In order to achieve a space velocity with the monolith catalyst lower than that used for the base case, a second catalyst was added to each side of the engine, in series with the original catalysts. This halved the space velocity, but also doubled the amount of noble metal in the system.

V.3.3.2.1 Gaseous Emissions

Halving the space velocity and doubling the noble metal content had a clearly beneficial effect on CO and HC emissions, lowering the average FTP values to 1.5 and 0.13 g/km for CO and HC respectively, as shown in Appendix Table E-10, from base case values of 2.7 and 0.29.

V.3.3.2.2 Sulfate Emissions

Sulfate emissions from the FTP runs were lowered, compared to the base case, by this decrease in space velocity. This is all the more surprising in view of the doubling of noble metal compared to the base case. The average for the double catalyst configuration is 0.015 g/km, while the base case was 0.025 for the 0.032 wt. % sulfur fuel. These lower results are directionally consistent with the effect of increasing space velocity, found with the pellet car to increase sulfate emissions. One possible explanation for these seemingly anomalous findings has already been discussed in Section V.3.3.1.2, namely, that under FTP conditions at least, sorption of sulfate on the catalyst substrate is the determining factor for tailpipe emissions rather than the kinetics of sulfate formation over the catalyst. Since sorption rate should increase with decreasing space velocity, then, under this theory even though the rate of formation is increasing at lower space velocities, the rate of sorption is increasing even faster, resulting in a net decrease in tailpipe emissions.

At 96 km/h cruise, the average sulfate emissions over the two hour test interval was 0.055 g/km, compared to 0.050 for the base case with the same fuel. There seemed to be a more pronounced sulfate spike during the first half hour, due perhaps to the greater sulfur storage capacity of the doubled catalyst beds compared to the base case. A drop in SO2 emissions, leading to a fall-off in total sulfur balance from an initial 111% to a final FTP value of only 52%. This is at variance with the base case result, where first and last FTP sulfur balances were similar, and no explanation is available.

During the two hour 96 km/h cruise, the average sulfur balance was 109%, in good agreement with the 113% shown in Appendix Table E-6 for the base case.

V.3.4 Effect of Catalyst Noble Metal Composition

This report has already discussed the gaseous and sulfur oxide emission characteristics of vehicles equipped with monolith or pellet catalysts containing Pt-Pd mixtures as their active metals. In this section, we will discuss the behavior of similar catalysts, but containing only Pt.

The Pt-Pd monoliths were replaced with similarly sized experimental monoliths, at the same metal loading but containing only Pt. After the standard aging and preconditioning steps, the Pt catalyst was put through the test sequence for gaseous and $SO_4^{=}$ emissions.

For the pellet comparisons, it was necessary to switch from the standard 4.25 litre (260 in^3) converter supplied with the production car to a 2.6 litre (160 in^3) converter. An experimental Pt pellet catalyst was made available by a catalyst manufacturer, but there was insufficient quantity to fill the larger reactor. Therefore, the Pt versus Pt-Pd comparison was made with the smaller reactor used for both catalysts. A discussion of residence time effects themselves was given in Section V.3.3, and the shorter residence times here should not affect the pellet comparisons discussed in their section.

V.3.4.1 Pelleted Catalyst Vehicle

V.3.4.1.1 Gaseous Emissions

This system must be compared with the pelleted car described in Section V.3.3.1, since both use the small 2.6 litre catalyst canister. The only difference between the two sets of runs is the noble metal composition; Pt here and Pt-Pd in Section V.3.3.1. Noble metal loading remains the same. The FTP gaseous emissions shown in Appendix Table E-11 are, on average, 2.4 g/km CO and 0.13 g/km HC. These are slightly higher than the 2.0 for CO reported in Section V.3.3.1 for the Pt-Pd catalyst, but slightly lower than the 0.16 g/km found for HC emissions. Both quantities are subject to considerable uncertainty in the course of FTP testing, and a more sensitive indicator of small activity differences is probably presented by the steady state 96 km/h cruises. The Pt catalyst averaged 0.05 g/km CO and 0.012 g/km HC over this driving mode. The Pt-Pd showed 0.07 g/km CO and 0.019 g/km HC. There appears then to be a slight advantage for the Pt, although not enough to greatly influence the FTP runs.

V.3.4.1.2 Sulfate Emissions

As with nearly all pellet catalyst test sequences, here too the initial FTP showed higher sulfate emissions than the final one, which follows the 96 km/h cruise. In this case, the values were 0.034 g/km and 0.007 respectively. The initial value was higher than the comparabl run with the Pt-Pd catalyst, but the final FTP runs were similar for the two catalysts.

At 96 km/h cruise conditions, a larger initial spike of sulfate was seen with the Pt catalyst, but the subsequent emissions were comparable to those from the Pt-Pd catalyst. This larger release of sulfate during the beginning of the cruise could be indicative of more sulfate being produced, and stored, during the preceding lower speed driving modes. As will be seen below, the SO_2 release results tend to confirm this hypothesis.

V.3.4.1.3 Sulfur Dioxide Emissions

The bubbler values for SO_2 emissions during the two FTP runs are equivalent. However, the much greater sulfate release during the first FTP yields a total sulfur balance of 40%, compared to only 22% for the final FTP. The most striking feature is the high level of SO_2 release during the cruise mode. On an overall average, taking the integrated bubbler value of 143% for SO_2, and the average of the four filter sulfate samples, the total sulfur balance is 207%. It is clear from the TECO reading for the first half hour, as well as the first filter sample, that much of this SO_x excess is released during the beginning of the cruise.

The magnified storage-release phenomenon seen with this Pt catalyst, compared to its Pt-Pd counterpart, may be due to several factors. Platinum may be more active than Pt-Pd for conversion of SO_2 to sulfate, especially at low speed driving modes. This, in turn, could lead to more storage on the catalyst, since sulfate should react with the substrate more easily than does SO_2. Then under higher speed and temperature driving modes, this extra sulfur is released. Alternatively, the storage-release effects may be related to the catalyst substrate itself. The two catalysts compared here were made by two manufacturers and, in addition to their noble metal changes, may have different quantities and types of substrate or manufacturing techniques. Not enough information is available to confirm these speculations, nor even to confirm if the observed storage-release behavior differences are real.

V.3.4.2 Monolith Catalyst Vehicle

V.3.4.2.1 Gaseous Emissions

The two FTP runs, shown in Appendix Table E-12, gave average CO and HC emissions of 1.9 and 0.18 g/km respectively, considerably lower than the values of 2.7 g/km for CO and 0.29 g/km for HC found with the Pt-Pd catalyst in the base case tests reported in Section V.3.1.2.1. Because of the uncertainties inherent in FTP gaseous emission results, the steady state emissions at 96 km/h cruise were also compared to determine if an activity difference between the two catalysts existed. The Pt catalyst averaged 0.08 g/km for CO and 0.01 g/km for HC. In contrast, the Pt-Pd catalyst averaged 0.21 g/km CO and 0.03 g/km HC. There appears then to be a real activity advantage for the Pt catalyst.

V.3.4.2.2 Sulfate Emissions

In contrast to the four Pt-Pd base case FTP runs with 0.032 wt. % sulfur fuel, the two FTP runs with the Pt catalyst were not similar. Here the final FTP value of 0.042 g/km was significantly higher than the initial value of 0.024. Together they averaged 0.033 g/km, compared to the Pt-Pd catalyst average of 0.025. In addition, the 20 minute idle period yielded 0.20 g for the test, compared to only 0.03 g for the idle period with the Pt-Pd catalyst. On the other hand, at 96 km/h cruise, the Pt catalyst averaged only 0.042 g/km, compared to 0.051 for the Pt-Pd sample. It would appear from these results that the Pt catalyst may produce slightly more sulfate at lower speed driving and slightly less at high speed driving than does the Pt-Pd catalyst.

V.3.4.2.3 Sulfur Dioxide Emissions

The two FTP runs showed similar SO_2 release characteristics, typical of monoliths. The overall sulfur balances were somewhat higher for the final FTP, however, because of the larger sulfate release. The bubbler value for the 96 km/h cruise, combined with the four half hour filter sulfate samples, gave an average sulfur balance of 94%, with no apparent trend with time, based on the TECO and filter values.

V.3.5 Effect of Changes in Catalyst Operating Temperature

The effect of catalyst operating temperature on $SO_4^=$ production has been investigated on our two test vehicles. The car tests involved raising the operating temperature of a pelleted catalyst by insulating and heating the exhaust pipe upstream of the converter and retarding spark timing, and lowering the monoliths' operating temperature by moving them back about 100 cm from their normal post-manifold position and externally cooling the exhaust lines. In all other respects, the vehicles were similar to their basic configurations.

In the pellet test, the maximum catalyst outlet temperatures were raised by 110°C, from 450°C to 560°C, for the FTP. At 96 km/h cruise, an identical rise was observed, from 620°C to 730°C. The monolith maximum temperatures were lowered from the normal 610°C to 510°C during the FTP. For the cruise mode, the maximum temperature dropped from 645°C to 540°C. In all other respects, these tests were conducted in the same way as were the base case runs, with Pt-Pd catalysts and 0.032 wt. % sulfur fuel.

V.3.5.1 Pellet Catalyst Vehicle

V.3.5.1.1 Gaseous Emissions

The two FTP runs differed considerably in CO emissions, due probably to some undetected variations in the vehicle operation during cold-starting. The only thing that can be said is that the average CO emissions, 2.0 g/km, were similar to the base case value of 2.3. It is not possible from this to tell if the higher operating temperature significantly improved CO conversion. The cruise results, averaging 0.024 g/km, were also slightly lower than the base case cruise average of 0.031. Emissions of HC, however, did show a large decrease at higher temperature. The two FTP results averaged 0.09 g/km, compared to 0.18 for the base case. At cruise, the higher temperature case yielded an average of only 0.004 g/km, compared to the base case average of 0.018. The greater effect of temperature on HC emissions than CO emissions is not surprising, given the easier homogeneous oxidation of the former.

Since the spark was retarded for this test, NO_x emissions also came down, to an average of 1.5 g/km for the FTP, from the base case average of 2.2.

V.3.5.1.2 Sulfate Emissions

The two FTP runs, as illustrated in Appendix Table E-13, showed the usual pattern of higher sulfate emissions on the first, and lower on the last FTP. Their average value of 0.007 g/km was not significantly different than for the four base case FTP runs with the same fuel, 0.006 g/km. The cruise results also showed the usual pattern for pellet catalysts during cruise, a high spike initially, which levels off thereafter. Neither the height of the spike, nor the two hour average, 0.055 g/km, differed from the base case, which had an average of 0.051.

V.3.5.1.3 Sulfur Dioxide Emissions

In contrast to the four base case FTP runs with the 0.032 wt. % sulfur fuel, which showed similar SO_2 desorption properties, regardless of whether they were first or last in the test sequence, at the higher operating temperature condition the first FTP resulted in a much higher rate of SO_2 release than did the final FTP. The initial high temperature FTP released somewhat more SO_2 than did the lower temperature FTP runs, while the final FTP was much lower than the base case results. Combined with their respective sulfate filter results, these two FTP runs showed sulfur balances of 47 and 7%.

At cruise, the bubbler results also showed a higher rate of SO_2 release than for the lower temperature base case. Combining the SO_2 with the average sulfate for the four half hour filters gives an overall average total sulfur balance of 163%. Although the total sulfur release occurring during the first FTP and the cruise are slightly higher than for the base case sequences, they don't seem sufficiently high to have cleaned off the catalyst enough to account for the almost complete removal of sulfur from the exhaust that occurred during the last FTP.

V.3.5.2 Monolith Catalyst Vehicle

V.3.5.2.1 Gaseous Emissions

Lowering the operating temperature during the FTP had a harmful effect on CO emissions, but not apparently on HC emissions. Values of 3.8 and 0.32 g/km respectively were obtained, as shown in Appendix Table E-14, compared to 2.8 and 0.30 for the higher temperature base case FTP runs.

Neither the CO nor HC emissions during cruise were affected, for the monolith catalyst, by lowering temperature. The base case values, at a temperature of about 645°C, averaged 0.21 g/km CO and 0.03 g/km HC. In this test, at a temperature of about 540°C, the emission values were 0.23 and 0.03 g/km.

V.3.5.2.2 Sulfate Emissions

The FTP sulfate emissions at the lower temperature showed a sharp drop compared to base case results, averaging only 0.010 g/km with 0.032 wt. % sulfur fuel, compared to 0.024. In addition, the initial FTP run was only half the level of the final run, whereas the base case sequences had shown uniformity between first and last FTP runs.

At cruise, however, temperature did not have a significant effect on sulfate emissions, averaging 0.055 g/km compared to 0.051 at the higher temperature base case.

V.3.5.2.3. Sulfur Dioxide Emissions

At the lower temperature, the two FTP runs showed SO_2 releases comparable to the base case, as were the total sulfur balances of 77 and 83% for the first and last runs. At cruise, however, the SO_2 release was only about half that produced at the higher temperature, with a resulting total average sulfur balance of only 84%, compared to 113% for the base case. Such a showing of comparable sulfur storage at low speed driving modes, and less release at high speed, could indicate a higher steady state catalyst sulfur content is achieved at lower operating temperatures.

V.3.6 Effect of Higher Noble Metal Loading

The catalysts used for the studies discussed so far were, as far as known, of similar metal loadings for each type. That is, the various monoliths had the same loading, and so did the various pellet samples. In this section, we will discuss a test aimed at determining if noble metal loading plays a role in $SO_4^=$ formation over the catalyst. The standard pelleted catalyst vehicle results shown in Section V.3.1.1 were compared with results obtained by emptying the 4.25 litre catalyst container and refilling it with another batch of Pt-Pd catalyzed pellets, which contained a 60% greater concentration of noble metal. It is believed the two contents were about 1.5 and 2.4 grams per vehicle. The higher loading catalyst was designed for use in the smaller, 2.6 litre canister, it being desired in commerical applications to use the same total amount of noble metal per car, regardless of catalyst canister size. A similar experiment was not possible with monolith catalysts because of the then unavailability of such catalysts at different metal concentrations.

V.3.6.1 Gaseous Emissions

No significant effect was found on FTP emissions of CO and HC. Although the initial and final FTP runs varied, due to run-to-run variation, their average values of 2.0 and 0.16 g/km for CO and HC respectively, as shown in Appendix Table E-15, were similar to the base case values of 2.3 and 0.18. Under cruise conditions, however, the CO and HC emissions were somewhat lower than the base case results, averaging 0.024 g/km CO and 0.012 HC compared to 0.031 and 0.018.

V.3.6.2 Sulfate Emissions

Sulfate emissions were also similar to the base case results. The initial FTP gave higher values than the final, and together they averaged 0.008 g/km, compared to a base case average of 0.006 g/km. At 96 km/h cruise, the initial spike was seen, and the average of 0.066 g/km was not significantly different than the base case average of 0.061 g/km with the 0.032 wt. % sulfur fuel.

V.3.6.3 Sulfur Dioxide Emissions

As with gaseous and sulfate emissions, not much difference was noted from the base case. Sulfur dioxide emissions were slightly lower during the FTP runs, with a resultant lower overall sulfur balance, but the effect is not deemed large. During the 96 km/h cruise, almost identical sulfur balances were achieved for this run and the base case runs.

V.3.7 Effect of Catalyst Aging

It is well known that automotive oxidation catalyst activity for CO and HC tends to decrease as the catalyst ages. A series of runs were made to determine if the activity of such catalysts changes with age for SO_2 oxidation. In addition, the sulfur oxides storage properties of aged catalysts were compared with those of fresh catalysts.

The standard vehicles were modified for these tests by replacing their low mileage monolithic and pelleted catalysts with similar catalysts which had seen previous service for at least 40,000 km. The aged pair of monoliths had seen respectively 41,400 and 49,000 km. The former had been run using fuel containing 0.025 g/litre of lead over the AMA cycle. The latter was operated for 45,000 km, also on the AMA cycle, with lead sterile fuel, then 480 km with fuel at 0.125 g/litre of lead, and finally 3500 km on lead sterile fuel again, which restored its CO and HC activity substantially to the pre-lead level. The aged pelleted catalyst had been mounted on a car driven 40,000 km on the AMA durability cycle, using fuel containing 0.0075 g/litre lead.

The pelleted catalyst, after aging, showed no increase in FTP gaseous emissions, but did have a 33% drop in sulfate emissions. The monolith catalyst also showed no change in FTP gaseous emissions with aging, but a large decrease in sulfate emissions, about 15%. It appears then that predictions of sulfate emissions from the total vehicle population, which have been based on measurements from fresh prototype or certification cars, will overestimate the levels from a population of normal age distribution.

V.3.7.1 Pellet Catalyst Vehicle

V.3.7.1.1 Gaseous Emissions

As shown in Appendix Table E-16, the aged pellet catalyst was tested under both turnpike and city driving preconditioning modes since these sequences were run early in the program before the decision was made to concentrate on the former preconditioning mode. The average CO emissions for the four FTP runs was 1.9 g/km and for HC, 0.18. These are very similar to the base case values of 2.3 and 0.18. Although not directly comparable, since the catalysts used here and that for the base case were different, these results indicate that 40,000 km of aging under the conditions employed here had little or no effect on FTP emissions of CO and HC. A more sensitive test, steady state activity at 96 km/h cruise, showed average CO emissions of 0.09 g/km, compared to the base case average of 0.03. Emissions of HC were 0.03 g/km, against the base case average of 0.02. These results show that some activity loss did occur upon aging, although not enough to influence FTP results.

V.3.7.1.2 Sulfate Emissions

Although FTP gaseous emissions were equivalent for the fresh and aged catalyst samples, sulfate emissions showed a decrease due to aging. The familiar pattern of higher initial FTP results was seen for each test sequence, but the absolute values were generally lower. Therefore, the overall average was only 0.004 g/km, compared to the base case of 0.006. Under cruise conditions, the sharp initial spike was observed, but again absolute levels tended lower. The overall averages were 0.049 g/km for the aged catalyst and 0.061 for the fresh.

V.3.7.1.3 Sulfur Dioxide Emissions

The two initial FTP runs show SO_2 emissions comparable to the base case, as are their overall sulfur balances. However, for some reason not understood, the final FTP runs gave significantly lower sulfur balances than their fresh catalyst counterparts. It would seem that the aged catalyst, after "cleaning" by the high speed cruise, has a greater tendency to remove sulfur oxides from the exhaust gas than does a fresh catalyst. Perhaps the catalyst surface has been roughened, providing more area for sulfur oxide sorption.

During the 96 km/h cruise, however, no more SO_2 is released from the aged catalyst than from the base case fresh catalyst, averaging 99% from the former and 91% from the latter. Overall sulfur balances are also similar, averaging 134% for the two aged catalyst test sequences and 139% for the two fresh catalyst sequences run with the 0.032 wt. % sulfur fuel.

V.3.7.2 Monolith Catalyst Vehicle

V.3.7.2.1 Gaseous Emissions

The FTP emissions of CO and HC from the aged catalysts, shown in Appendix Table E-17, were similar to those from the fresh monoliths. The four runs gave an average of 2.9 g/km CO and 0.28 g/km HC, compared to 2.7 and 0.29 for the base case. One of these runs, the initial FTP in the test sequence which followed city driving preconditioning, appeared to go unusually rich, as evidenced by its unusually high CO and HC and low NO_x emissions. This appeared to affect SO_2 and sulfate emissions also, as will be discussed below.

Although no difference was observed in FTP gaseous emissions between fresh and aged catalysts, as discussed previously, the FTP is not as sensitive an indicator of catalyst activity as is steady state operation. The two 96 km/h cruises with the aged catalysts showed average CO and HC emissions of 0.64 and 0.066 g/km respectively. In contrast, the four cruise modes run with the fresh catalysts had averages of only 0.21 and 0.033 g/km respectively, indicating some loss in activity for the aged catalysts.

V.3.7.2.2 Sulfate Emissions

The aged catalysts showed a significant drop in sulfate emissions, for both the FTP and cruise driving modes. The average of the four FTP runs was 0.009 g/km, compared to 0.025 for the fresh catalysts. At 96 km/h cruise, the comparison of the averages was 0.033 versus 0.051 g/km.

The highest FTP value, 0.014 g/km, corresponded to the one which seemed to be unusually rich based on its gaseous emissions, as discussed in the previous section. The next section will discuss a possible reason for this connection. It is also interesting that the first half hour cruise segment following this rich FTP run was unusually high in sulfate emissions, 0.053 g/km.

V.3.7.2.3 Sulfur Dioxide Emissions

Of the four FTP runs, again the rich run gave anomalous results, in this case unusually high SO_2 emissions, corresponding to 144% of the fuel sulfur consumed. In contrast, the other three runs ranged from 72 to 97%. Again, excepting the anomalous run, total sulfur balances ranged from 75 to 102%. The anomaly was 152%.

During the two cruise modes, the total sulfur balances, obtained from the bubbler values for SO_2 and the averaged filter samples for sulfate, were 112 and 125%. The latter includes the one high half-hour segment immediately following the rich FTP run. These values, both for the cruises and FTP runs are in generally good agreement with the results from the fresh catalysts, indicating aging had little effect on the relatively small storage properties of monolith catalysts.

The enriched carburetion during the anomalous FTP run may have contributed to the unusually high level of SO_2 release observed. To the extent the carburetor abnormality persisted into the cruise mode, it may have caused additional SO_2 release then also. The TECO results do indicate that the first half hour of this cruise released twice as much SO_2 as the subsequent intervals. The effect of enrichment on sulfur release from catalysts is not surprising in itself. It was observed previously in the tests run with pelleted catalyst and limited excess air, Section V.3.2.1. However, in that instance, while SO_2 and total sulfur release was going up, sulfate decreased sharply. In the present case, sulfate increased along with SO_2. Of course, the major difference between the two runs is the full time use of an air pump in this monolith run. It may be that in the presence of sufficient excess oxygen, the additional CO can still trigger catalyst release of sulfur, but more of the freed SO_2 can now be converted to sulfate during its passage through the catalyst bed.

V.3.8 Thermal Decomposition of $Al_2(SO_4)_3$

Because of the importance of sulfur release from oxidation catalysts, presumably through the decomposition of $Al_2(SO_4)_3$, several runs were made in a laboratory set-up, described in Section VI.4.1, in an effort to learn more about the mechanism of this reaction. In one run, a 13 cm^3 charge of pellets, made from pure $Al_2(SO_4)_3$, was placed in the tube reactor. A synthetic exhaust gas, identical to that detailed in Section IV.4.1 was used, at a space velocity of 100,000 v/v/hr., except that no SO_2 or sulfate was added. Water of hydration was driven off, and the material then heated progressively to 370, 480, 590, and 700°C. At each temperature, the SO_2 was monitored, with the TECO unit described in Appendix B, until it reached a constant level. Measurements of H_2SO_4 were then made for a one hour period with the Goksøyr-Ross method, also described in Appendix B, Section B.2.3. Table V-2 shows the results. It is seen that the quantity of sulfur released increases with temperature, which is not surprising. What is unexpected is the rapid increase in the ratio of sulfate to SO_2. Given the equilibrium relationship between SO_3 and SO_2, which shows that SO_3 decomposes with increasing temperature (Appendix Figure A-1), just the opposite ratio change would be predicted.

Table V-2

Thermal Decomposition of Aluminum Sulfate

3.2 mm $Al_2(SO_4)_3$ pellets Space Velocity = 100,000 v/v/hr.

Synthetic Exhaust Gas Composition: 12% CO_2; 12% H_2O; 3% O_2; Balance N_2

Temperature, °C	SO_2 Concentration, ppm	$SO_4^=$ Concentration, ppm	SO_3/SO_2 Found	SO_3/SO_2 Equilibrium
370	1.0	1.3	1.3	---
480	2.0	5.3	2.6	∿20
590	2.5	23.7	9.5	∿ 2.3
700	10.0	133	13.3	∿ 0.5

These results can probably best be explained by assuming that the $Al_2(SO_4)_3$ is not decomposing by the straight thermal mode;

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$$

but rather by a hydrolysis mechanism, given the high concentration of H_2O in the synthetic exhaust gas;

$$Al_2(SO_4)_3 + 3H_2O \rightarrow Al_2O_3 + 3H_2SO_4$$

Thus the initial release of sulfate from the $Al_2(SO_4)_3$ is not regulated by the SO_3/SO_2 equilibrium relationship, but rather the equilibrium for steam hydrolysis, which can explain the relatively high concentrations of sulfate.

Of course, once produced at high temperatures, there is a thermodynamic driving force for the decomposition of H_2SO_4;

$$H_2SO_4 \rightarrow H_2O + SO_3$$

The equilibrium curve in Appendix Figure A-2 shows that at a temperature as low as 400°C, only about 10% of the H_2SO_4 will remain undissociated. With H_2SO_4 decomposition yielding free SO_3, it would now be expected that the SO_3/SO_2 equilibrium would take over and lead to a rapid rise in SO_2 concentration, especially at the higher temperatures. The fact that this was not observed leads to the conclusion that the hydrolysis reaction is controlling and that probably the decomposition of SO_3 to SO_2 does not occur rapidly enough to establish the equilibrium ratio in the short residence time available before the sampling train.

It should be borne in mind, of course, that these results were obtained with pure $Al_2(SO_4)_3$, in the absence of any catalyst. In the case of a vehicle oxidation catalyst, where the $Al_2(SO_4)_3$ would be in close contact with active metal catalyst surfaces, it is likely that the $SO_3 \rightarrow SO_2$ reaction rate would be enhanced during the reaction products release from the catalyst bed, and a SO_3/SO_2 ratio closer to the equilibrium value would be measured.

VI. Task IV - Feasibility Studies of Sulfate Removal From Exhaust Gas By Traps

This task consisted of a feasibility study of the use of a solid sorbent trap, located in the exhaust system downstream of the oxidation catalyst, for removal of sulfate from the exhaust gas. The program consisted of both vehicle studies of the durability and performance of such traps and laboratory screening of potential sorbent materials. Four vehicle tests were run for intervals up to 42 000 km. The sorbent particles used were the following:

- 85% CaO/10% SiO_2/5% Na_2O pellets
- 85% CaO/10% SiO_2/5% Na_2O rings
- $CaCO_3$ chips
- ZnO pellets

These and a number of other candidate sorbent materials were also screened for sulfate removal activity, under several operating conditions, in a laboratory reactor. The materials tested, in addition to the above, were:

- Al_2O_3
- BaO
- 80% CaO/20% SiO_2
- ZnO
- $CaSiO_3$
- $Ca(OH)_2$
- CaO
- $CaCO_3$
- MnO_2
- MgO
- $MgCO_3$
- 85% MgO/10% SiO_2/5% Na_2O
- ZrO_2

VI.1 Summary of Results

VI.1.1 Vehicle Tests

A total of four vehicle durability runs were made, using oxidation catalyst-equipped vehicles with trap canisters containing 85 CaO/10 SiO_2/ 5 Na_2O (benchmark), ZnO and $CaCO_3$. The benchmark material* was used in the form of both pellets and rings. The benchmark pellet test was run for a total of 42 000 km. It was found that nearly all of the sulfate was removed from the exhaust during this test, as well as a significant fraction of the SO_2. Total particulate and calcium emissions were also low, indicating little attrition of the sorbent. However, pressure drop build-up in the trap was impracticably large, rising from an initial value of about 1 000 pascals to a final value of 30 000 pascals.

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* This material was found, during prior company-sponsored work, to be very active for sulfate sorption and has since been used as the standard against which other sorbents are evaluated.

The benchmark material was also fabricated into rings, offering a greater void volume than the pellets. As a result, pressure drop through the trap increased at a slower rate than in the case of the pellets, 500 pascals initially and 4 000 after 20 000 km. However, the sorption efficiency for sulfate was adversely affected. Initial values were only 80%, falling to 30% after 15 000 km. The $CaCO_3$ chips and ZnO pellets were tested for distances of 10-17 000 km and had little or no sulfate pick-up.

VI.1.2 Laboratory Screening

VI.1.2.1 Sorbent Activity

A number of sorbent candidates, which appeared to meet all or most of the criteria for such materials, as described in Task I, were tested for SO_2 and sulfate pick-up efficiency in a laboratory reactor using synthetic exhaust gas.

It was found that several forms of Al_2O_3, as well as the 80% CaO/20% SiO_2 preparation, were much inferior to the benchmark sorbent; the former because of poor sorption efficiency, the latter because of a lack of physical strength. The CaO-SiO_2 was prepared by calcination of a dry mix prior to pilling. Barium oxide was a complete failure, due to hydration and subsequent dissolution of the hydroxide in its own water of hydration. Another material giving poorer results than the benchmark sorbent was $CaCO_3$. A number of materials were found to have activity equivalent to the benchmark, at least for short periods of time. In addition, they showed generally lower activity for [illegible] removal, a desirable feature. These sorbents included ZrO_2, $CaSiO_3$, CaO, MnO_2, and several MgO-based samples. Only the calcium-based materials, however, are free from the disadvantage of forming water soluble sulfates.

VI.1.2.2 Effect of Operating Conditions on Sorption Efficiency

In addition to the temperature used for the bulk of the sorbent screening runs, 480°C, several runs were also made at 370°C. Magnesia, ZnO, and the benchmark sorbent did not show a significant activity change, but the ZrO_2 sample did.

Screening runs were also carried out at space velocities other than the standard of 100,000 v/v/hr. Values of 150,000 and 50,000 were used, and in some runs the 370°C temperature was also used. At 150,000 v/v/hr and 480°C, the benchmark sorbent showed no apparent loss of activity, but MgO and ZnO both showed some loss due to decreased contact time. At this higher space velocity and 370°C, the benchmark sample still showed no loss in sorption efficiency. Magnesia showed some loss.

Finally, at 50,000 v/v/hr and 480°C, results for benchmark sorbent, MgO and CaO were similar to those at 100,000 v/v/hr, indicating little or no effect of increasing residence time. One exception was greater SO_2 pick-up by the CaO sample.

VI.2 Vehicle Durability Tests of Traps

VI.2.1 Experimental Procedures

VI.2.1.1 Vehicle Preparation

Vehicle tests were conducted on two 351 CID V-8 Fords, a 1973 and a 1974 model. They were equipped by us with two Engelhard PTX-IIB® Pt-Pd monolith oxidation catalysts, one on each bank of the engine in the post-manifold position. Air pumps were also added. The traps themselves consisted of conventional 4.25 litre canisters, designed for use with pellet catalysts. They were emptied of their original catalyst charge and refilled by us with sorbent particles. The traps were placed in the exhaust system under the rear seat and the standard mufflers removed.

VI.2.1.2 Test Fuels

Essentially all of the kilometer accumulation and testing done in this task were conducted with the 0.032 wt. % sulfur content fuel described in Section V.2.2.

VI.2.1.3 Test Procedure

Kilometer accumulation was accomplished on automatic dynamometers, using the AMA durability cycle. Periodically, the vehicles were emissions tested using the Exxon Research exhaust particulate sampler described in Appendix B. Initially, measurements were made at 64 kph cruise conditions only, using two successive one hour intervals, but at the 17 600 km point of the first test (benchmark pellets), a hot start 1975 FTP was added after the two one hour cruises. Measurements were made of total particulate, total sulfate, and total calcium (or zinc) emissions, as well as pressure drop across the trap for each cruise mode. During the hot start FTP runs, these three particulate measurements, as well as gaseous emissions of CO, HC, and NO_x were recorded. Fuel economy and SO_2 emissions were also measured during each test mode. The results for each of the four durability runs are recorded in Appendix Tables E-18 to E-21.

VI.2.2 85 CaO/10 SiO_2/5 Na_2O (Benchmark) Pellets

The initial vehicle durability run was made using 3.2 mm cylindrical pellets made from this material, which had been identified during an earlier Exxon Research program as an active sorbent for sulfate.(8) It has been designated benchmark sorbent, since other sorbent's activity is evaluated against this material.

VI.2.2.1 Benchmark Preparation

VI.2.2.1.1 Powder Preparation

The starting material for the benchmark pellets was made by the following procedure, using these materials:

- Calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$, reagent
- Kieselguhr, calcined
- Sodium metasilicate $Na_2SiO_3 \cdot 9H_2O$, reagent
- Sodium hydroxide, reagent

1. Add 1700 gms of calcium nitrate to 6 litres of distilled water while stirring.

2. Slowly add 25 gms of calcined Kieselguhr.

3. Slowly add 118 gms of sodium metasilicate and stir constantly.

4. Dissolve 718 gms of sodium hydroxide in 750 ml of distilled water.

5. Add sodium hydroxide solution to 6 litre solution dropwise over ∿2 hours using a dropping funnel. Stir solution constantly.

6. After sodium hydroxide has been added, continue stirring for one additional hour.

7. Vacuum filter the mixture using two large, ∿16 cm diameter, Buchner funnels. Wash the filter cakes twice, each with 500 ml of distilled water.

8. Place cakes in large evaporating dishes and dry overnight in an oven @ 250°F.

9. Powder solid filter cakes to pass through 14 Tyler mesh screen.

VI. 2.2.1.2 Pellet Preparation

The screened, dried powder described in the previous section was compacted into pellets using a Stokes compacting machine, Model 900-512-1. This is a 16 station, rotary motion unit which allows upper and lower compaction. Punches and dies of 3.2 mm were used.

It should be noted that all machine settings cannot be quantified, and that the "best" settings for forming acceptable pills are obtained on a trial and error basis. There are three variables which the operator can control: speed of pilling, depth of die fill, and compaction pressure.

Qualitatively, the settings which resulted in the "best" pills were: speed of pilling at maximum (this had little or no effect on quality of pilling), depth of die fill near maximum (this powder was quite fluffy and could be greatly compacted), and compaction pressure set just below the point at which the over-pressure safety releases (1/8 ton/face). After pilling, the pills were calcined for four hours at 1200°F.

VI.2.2.2 Experimental Results

The results obtained with the experimental vehicle equipped with a sulfate trap containing benchmark pellets are shown in Appendix Table E-18. Prior to testing the sulfate trap, the vehicle without trap was run for 3,218 km on 440 ppm S fuel and tested for particulate emissions. The total particulate emission rate averaged 0.171 gm/km for two tests while the sulfate emission rate averaged 0.0858 gm/km. The test procedure was a one hour cruise at 64 km/h. For both runs, parallel filters showed very good weight correspondence.

The trap was then installed and the above test repeated with no accumulated mileage on the trap. The total particulate emissions for duplicate runs averaged 0.012 gm/km with sulfate emissions of 0.002 gm/km. This represents a reduction of 98% in sulfate emissions. Another duplicate set of 64 km/h tests was then made followed by different test cycles of one hour at idle and two hours at 96 km/h. For all test cycles, sulfate emissions were reduced by greater than 95%. During these tests a third parallel filter was collected and analyzed for calcium. In all cases, the calcium emission rates were very low indicating little or no sorbent attrition. Testing of a similar oxidation catalyst vehicle but without a CaO trap resulted in calcium emissions of 4×10^{-3} gm/km. Similar oxidation catalyst vehicles without traps and with sulfur free fuel produced total particulate emission rates higher than those observed with the trap vehicle. Therefore, it appears that the sulfate trap is removing other exhaust particulate in addition to sulfates.

After these tests, trap mileage was extended to 1,609 km by running on the AMA durability cycle. Duplicate one hour tests at 64 km/h were made at 1609 and 1786 trap kilometers. The results show low total particulate and sulfate emissions. At this point, the fuel was switched from the 480 ppm sulfur fuel to the 320 ppm S fuel. Results at 3,218, 4,827, and 6,436 trap kilometers showed, in all cases, that total particulate and sulfate emissions were very low, indicating the trap was active and not attriting.

While CaO is a very active sorbent, its volume increases significantly as it sulfates. Based on crystalline densities, the complete sulfation of CaO to $CaSO_4$ would produce a three-fold increase in volume. While the pellets are somewhat porous, they cannot accommodate such an expansion internally and must expand into the void volume of the bed. This expansion will cause the pressure drop across the bed to increase as sulfation increases. To examine this problem, pressure drops have been measured during the 42 km/h testing. A GM reactor filled with pellets of the same geometry as the CaO pellets typically exhibits a pressure drop of about 1,000 Pa (4 inches of water) at 64 km/h. The sulfate trap at 3 218 km showed a pressure drop of 9 950 Pa (40 inches of water) indicating expansion of the sorbent material. At 4 827 and 6 436 trap kilometers, the pressure drop remained relatively constant.

As trap testing continued at 64 km/h through 12 870 km accumulation, the sulfate, total particulate and calcium emissions remained low. Sulfate was 0.001 g/km and calcium at or near the detection limit of 3×10^{-5} g/km. Total particulate was 0.003 g/km at 9 650 km. The 12 870 km value was inadvertently lost due to experimental error. The pressure drop over this interval ranged between about 15 000 and 23 000 Pa (60-92 inches of water).

At 17 600 km, it was noted that the two successive 64 km/h cruise tests had reversed the order of total particulate emissions. Previously, the first test had shown lower levels, but at this point, and for the remainder of the test, the first cruise began showing higher levels. Sulfate and calcium emissions continued to remain about the same for the two cruises, however. To examine this problem, the metals filter used previously only for calcium analysis was analyzed for the following metals: lead, iron, copper, aluminum, zinc, chromium, and nickel. In all cases, the total metal emissions were higher for the first test. The iron emissions were the largest fraction. In most cases, the first cruise gave much higher iron values than the second. The lead emissions are also somewhat higher during the first test. Therefore, it appears that the metal emissions are responsible for the increased particulate emissions during the first test cycle with the iron emissions making up the largest fraction.

At the 17 600 km point, a hot start FTP was added to the test sequence to assess the effects of cyclic operation on emissions. It is seen in Appendix Table E-18 that at this and all subsequent test periods, the cyclic values for total particulate, sulfate, and calcium emissions were generally higher than for the cruise modes.

From 17 600 km to the final test interval at 42 400 km, the values for these three emissions did not increase. The only possible increase was recorded for calcium emissions at the final measurement point. Pressure drops, however, continued to rise, reaching as high as 29,000 Pa (116 inches of water) at the end. It should be noted that the pressure drop tended to change during the course of a cruise, gradually falling as water of hydration was driven from the sorbent. For example, at 42 400 km, the initial pressure drop for the first cruise was 37 500 Pa (150 inches of water), lowering to 29 000 Pa after about fifteen minutes.

Gaseous emissions of CO, HC, and NO_x showed no trend over the interval from 17 600 to 42 400 kilometers, taken during the hot start FTP runs. Fuel economy did decrease with increasing trap age, however, presumably because of the harmful effect of increasing back pressure. Initial fuel economy for the trap car at 64 km/h was about 8.6 km/litre, but fell to 6.0 km/litre at the end of the run. Similarly, the first FTP, at 17 600 km, gave an average fuel economy value of 4.2 km/litre, which fell to 3.9 at the conclusion of the run. Finally, SO_2 readings, taken before and after the trap with the TECO instrument described in Appendix B, showed approximately a 50% removal efficiency for this gas, holding steady throughout the run. It should be pointed out that the TECO had not been correctly calibrated as yet, so the absolute numbers in Appendix Table E-18 are not as reliable as are the before and after trap comparisons.

This durability test was terminated after 42 400 km, primarily because of the high pressure drop through the trap. Examination of the sorbent bed showed that the pellets, for the most part, had remained intact. They were, however, adhering one to another with some fines in the open areas. The volume expansion of the pellets was then determined by measuring ten random pellets of the fresh sorbent and ten random used pellets. The expansion was found to be 13% which would theoretically increase the pressure drop by a factor of 5. The fines would also plug the flow passages and increase this factor significantly. A number of analyses were performed on the pellets themselves and are described in the next section. A summation of the sulfate sorption efficiency and pressure drop build-up of the trap is presented in Figures VI-1 and VI-2.

VI.2.2.3 Chemical Analysis Of Used Pellets

Samples of the fresh and used sorbent material were analyzed to determine the mechanism of sulfation. A detailed report of the results of these tests appears in Appendix Section D.1. The first analysis was a determination of density and pore volume. The density and pore volume of the fresh sorbent show that the initial pellets had an internal void volume of 49%. This allowed deep penetration of the sulfur oxides into the pellets and also accommodated a large part of the sulfation volume expansion as shown by the decrease in void volume of the used pellets to 35%.

The bulk sulfate content of the fresh and used material was determined. The fresh material was less than 0.1% sulfate. The used material was ∿40% sulfate by weight. The sulfate gradient across the pellet was determined by selectively scraping pills at different diameters and analyzing the scrapings. The gradient was also determined by scanning electron microscopy - X-ray energy spectrum. The X-ray energy spectrum showed the following gradient:

FIGURE VI - 1

TRAP EFFICIENCY AT 64 KM/H—PELLETS

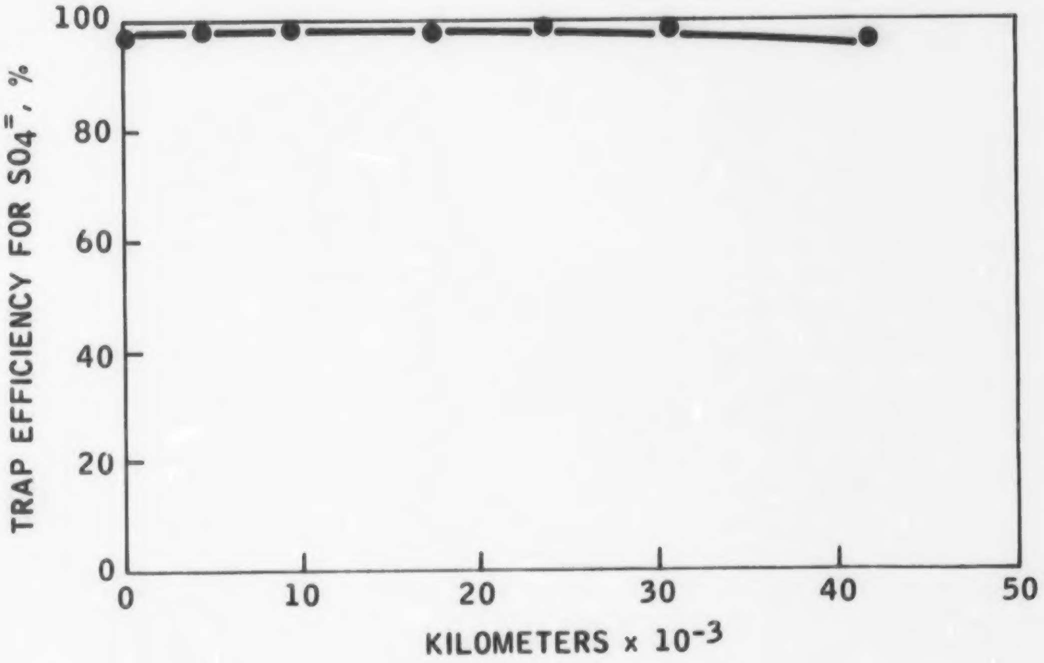


FIGURE VI - 2

PRESSURE DROP AT 64 KM/H—PELLETS

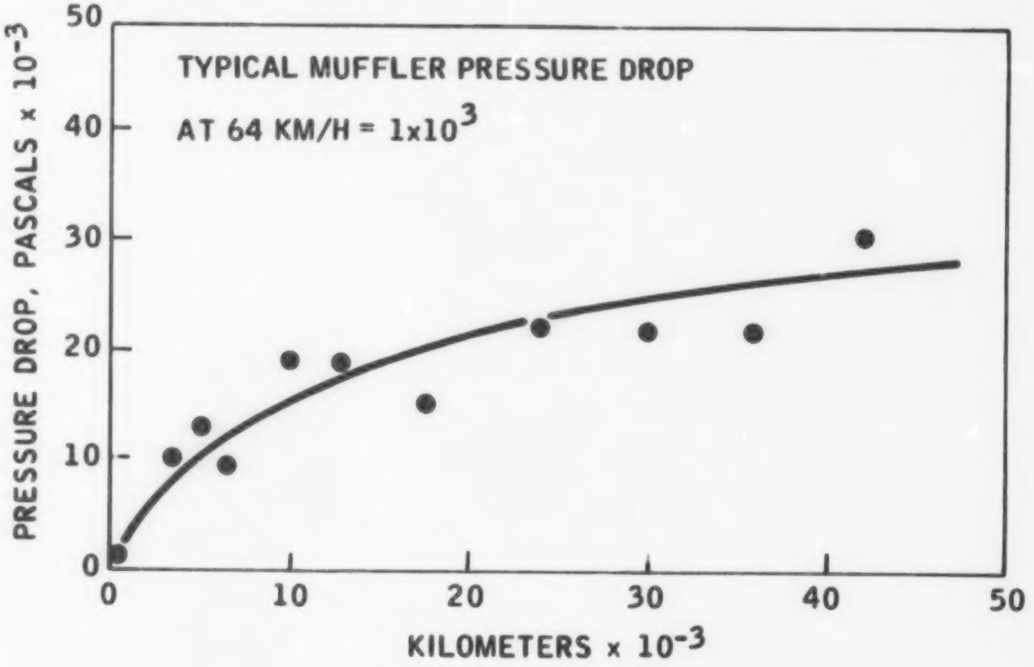


Table VI-1

Radial Distribution of Sulfur and Calcium in Used Trap Pellets

Radial Position	Sulfur Relative Peak Height	Calcium Relative Peak Height
1.0 (edge)	53	50
0.76	56	50
0.65	54	49
0.50	36	77
0 (center)	35	70

The relative peak heights are very nearly proportional to concentration. Both methods show the same gradient within experimental accuracy. These results are very important since they show that sulfation is taking place throughout the pellets.

Fresh and used samples were analyzed by X-ray diffraction to determine the crystalline compounds present. The fresh sample showed calcium oxide, calcium silicate hydrate ($Ca_2 SiO_4 \cdot H_2O$) and sodium carbonate hydrate ($Na_2 CO_3 \cdot 10H_2O$). The calcium silicate is due to reaction of the calcium oxide and silicon oxide during calcining. The sodium carbonate hydrate is due to the reaction of the sodium oxide with carbon dioxide either during calcining or in the interim between calcination and analysis followed by hydration.

The used samples showed a very large amount of calcium sulfate, some calcium oxide, calcium silicate hydrate, and sodium carbonate hydrate. These compounds would be expected given the compounds found in the fresh material with the exception of possibly the sodium carbonate. Thermodynamics favors the conversion of the carbonate to the sulfate. Due to the initial low concentration of sodium oxide, 5%, and the large amount of calcium sulfate, it would be very difficult to see sodium sulfate in the X-ray diffraction patterns. However, sodium carbonate was identified, indicating, at most, only partial formation of sodium sulfate.

VI.2.3 $CaCO_3$ Chips

Although the durability test of benchmark pellets showed favorable sulfate pick-up efficiency and capacity characteristics, the build-up of pressure drop was unfavorable. One possible method of overcoming this is through the use of a sorbent which expands less upon sulfation. Calcium carbonate increases in volume by only a factor of 1.4 upon sulfation, compared to an almost three-fold increase in the case of CaO. A price must be paid, of course, for this improvement in volume expansion. Because the starting molecule is now larger, the sorbent will have less capacity for sulfate sorption per unit of volume or weight than would CaO. Since our interest was basically in minimizing pressure drop, the same type of vehicle test described in Section VI.2.2 was repeated anyhow, this time using pure $CaCO_3$ as the sorbent in place of the benchmark material, which was primarily CaO.

VI.2.3.1 Test Conditions

Because of the hardness of $CaCO_3$, the sorbent particles were not pelleted from powder. Rather, marble chips were granulated and the 4/7 mesh fraction was used to simulate as closely as possible the 3.2 mm pellets used previously. The same car was used, but fresh monolith catalysts were mounted to provide maximum levels of sulfate in the exhaust. Surprisingly, however, the new set of catalysts gave only about one half the level of sulfate emissions as had the original catalysts when they were fresh (corrected to the 0.032 wt. % sulfur level fuel). Because of this discrepancy, and also because of the now realized effect of catalyst aging on sulfate production, it was decided to measure the sulfate emissions entering the trap, and compare these with the after trap filter results in order to calculate removal efficiency. The Goksøyr-Ross technique, described in Appendix B, was used to follow the before trap sulfate level of the exhaust gas. Because of its lack of constant volume sampling, it can be used only for the steady state cruise modes.

VI.2.3.2 Experimental Results

As shown in Appendix Table E-19, the sulfate sorption efficiency of this trap was quite poor. If the filter values of sulfate after the trap are compared with the baseline emissions, only about 16-55% pick-up is calculated, which varied randomly over the 17 400 km duration of the run. If the actual pre-trap sulfate values, obtained from the raw exhaust during each 64 km/h test by the Goksøyr-Ross method are used as the basis for comparison, essentially no sulfate sorption appears to be occurring. For reasons to be discussed in Appendix C, the Goksøyr-Ross method may tend to give low values. Therefore, we will assume the post-trap filter samples, compared to the base case sulfate emissions, as providing the correct value for sulfate sorption efficiency. In either case, though, the results are poor.

Over the course of the run, no trend was observed in total particulate emissions during cruise modes. The last FTP run did give the highest value, however. Calcium emissions themselves were at or near the detection limit for most of the tests, indicating little or no sorbent attrition.

The pressure drop showed no upward trend during this run, indicating that in the absence of significant sulfation, which would result in sorbent swelling, there is little or no tendency for pressure drop to increase.

Contrary to the benchmark pellets, the $CaCO_3$ chips did not cause a drop in vehicle fuel economy with aging, measured both at cruise and on the FTP. Again, this is undoubtedly because of the lack of pressure drop build-up. Actually, there was an improvement with time of fuel economy, but this was probably due to other vehicle changes unrelated to the trap. Gaseous emissions showed no significant trend with time. No measurements were made of SO_2 sorption, but in view of the low level of activity for sulfate, this would not be expected to be large.

Because of the disappointing sulfate sorption performance, the test was discontinued at the 17 400 km mark. It is not known if the poor reactivity is inherent in CaCO3, or was due to the very dense, non-porous nature of the chips used. As will be seen in Section VI.4.2.2, similar chips did show some activity in laboratory screening runs.

VI.2.4 ZnO Pellets

The next durability test was conducted with the same vehicle used for the $CaCO_3$ chips, with fresh catalysts installed. The trap was filled with 5 mm extrudates of ZnO, a catalyst material manufactured by the Harshaw Chemical Company.

VI.2.4.1 Experimental Results

The car was first baselined, with the trap empty of sorbent. These results are shown in Appendix Table E-20. At 64 km/h cruise, the total sulfate emissions averaged 0.031 g/km, and total particulate 0.078 g/km. The subsequent cruise tests, after aging periods of 5 300, 9 700, and 15 900 km, averaged about a 30% removal of sulfate. Removal rates for total particulate averaged just over 50%. During the hot start FTP runs, however, no sulfate and little total particulate removal was found.

Readings of the SO_2 concentrations in the raw exhaust, before and after the trap, showed that no SO_2 sorption was occurring, not surprising in view of the poor sulfate activity. It was also found that the level of zinc particulate emissions was significantly higher than that observed with any of the base case tests or tests with other sorbents. This indicates a high level of attrition for the ZnO sorbent. The pressure drop was lower initially than for either the benchmark pellets or $CaCO_3$ chips, which may be a reflection of the larger size of the ZnO starting material. The failure of the pressure drop to increase with time is again probably due to the lack of sulfation and consequent swelling.

VI.2.5 85 CaO/10 SiO_2/5 Na_2O Rings

As was discussed in Section VI.2.2, the benchmark pellets were very effective for sulfate sorption. However, they also swelled during sulfation which caused an unacceptably large increase in pressure drop. One possible method of minimizing this effect is through the use of particle shapes which offer inherently lower pressure drops than do pellets. Rings were selected for initial testing of this concept, using the benchmark powder as the starting material.

VI.2.5.1 Test Conditions

The benchmark powder was fabricated into rings of 1.58 cm O.D. x 0.48 cm I.D. and 0.79 cm height by Girdler Chemical, Inc. These dimensions were not the optimum choice for compromising pressure drop and surface area/volume parameters, but happened to be the size of dies available to Girdler at the time of our fabrication request.

A new vehicle was used for this run, but like the car used for the three previous durability runs, it was a full size, 351 CID V-8, with air pump and was equipped by us with two Engelhard PTX-IIB® monolith catalysts, one on each bank of the engine. As before, a 4.25 litre catalyst canister was emptied of its original charge, refilled with sorbent and placed in the exhaust system under the rear seat.

VI.2.5.2 Experimental Results

As shown in Appendix Table E-21, the benchmark rings were somewhat poorer than the benchmark pellets, Section VI.2.2, for sorption of sulfate. For the 64 km/h cruise tests, the absolute levels of sulfate emissions, over the first 7 660 km, averaged about 0.005 g/km, compared to 0.001 g/km for the pellets. On the basis of the base case emissions of 0.033 g/km, this equalled about 85% efficiency. However, with increasing kilometer accumulation, sorption efficiency began falling off sharply, as shown in Figure VI-3, with sulfate emissions rising to an average of 0.014 g/km at the end of the run at 20 400 km. Under the hot start FTP test condition, sulfate emissions did not show such a trend, and averaged about 0.007 g/km or 72% removal compared to the base case. Total particulate emissions for both types of tests followed the same general trend as did sulfate emissions. Calcium emissions were at or near the detection limit for the entire run.

Surprisingly, even during the early part of the run, when fairly high sulfate pick-up rates occurred, there was no pick-up of SO_2, as evidenced by comparing TECO readings of the undiluted exhaust before and after the trap. This indicates that the inherently good activity of the benchmark material for SO_2, at least in the pelleted form, is negated by the poorer gas-solid contacting efficiency of a ring bed. Since sulfate is a more active species than is SO_2, it is less affected by the drop in contacting efficiency. Directionally, this widening of the pick-up efficiency gap between sulfate and SO_2 is desirable, since SO_2 sorption is unnecessary and merely increases the rate of sulfation of the sorbent. In turn, this decreases its effective capacity for sulfate and increases the rate of swelling.

The trap pressure drop, as expected, was lower than for the pellets initially and also rose at a slower rate, as shown in Figure VI-4. Thus, at 3 000 km, the pressure drop was only about 600 Pa (2.4 inches of water) at 64 km/h cruise, and rose only to 4 200 Pa (∿17 inches of water) at 20 400 km. In contrast, the pellet bed had reached about 20 000 Pa (80 inches of water) by this time.

Gaseous emissions of CO and HC showed a sharp rise toward the end of the run, but it is not clear if this was due to a problem with the carburetor or the catalysts. If enrichment of the carburetion occurred, it was not reflected in the fuel economy, which remained constant over the entire run. On the other hand, a loss in catalyst activity for CO and HC should have been accompanied by an even greater loss in SO_2 oxidation activity, which, as was shown under Task III of this contract, is even more sensitive to catalyst activity. The evidence here is ambiguous. At 14 400 km, when the greatest CO value was recorded, there was no drop in sulfate emissions on the filter, nor even in pre-trap sulfate values measured by the Goksøyr-Ross method. At 20 400 km, where the highest HC value occurred, the Goksøyr-Ross measurement did show a drop in pre-trap exhaust sulfate concentration.

VI.3 Status of Sulfate Traps

Although good $SO_4^=$ trapping efficiency and capacity, and relatively low pressure drop have been demonstrated, it has not been possible yet to combine all of these necessary features into one structure. Pellets of the $CaO/SiO_2/Na_2O$ composition have met the efficiency and capacity criteria, but not the pressure drop requirements. Several

FIGURE VI - 3

TRAP EFFICIENCY AT 64 KM/H—RINGS

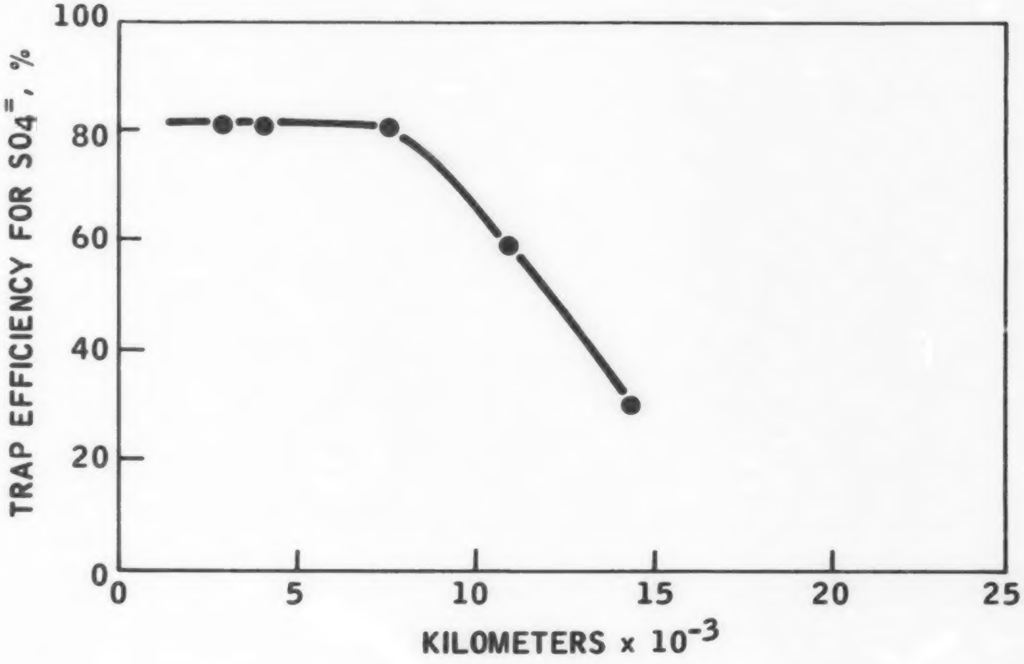
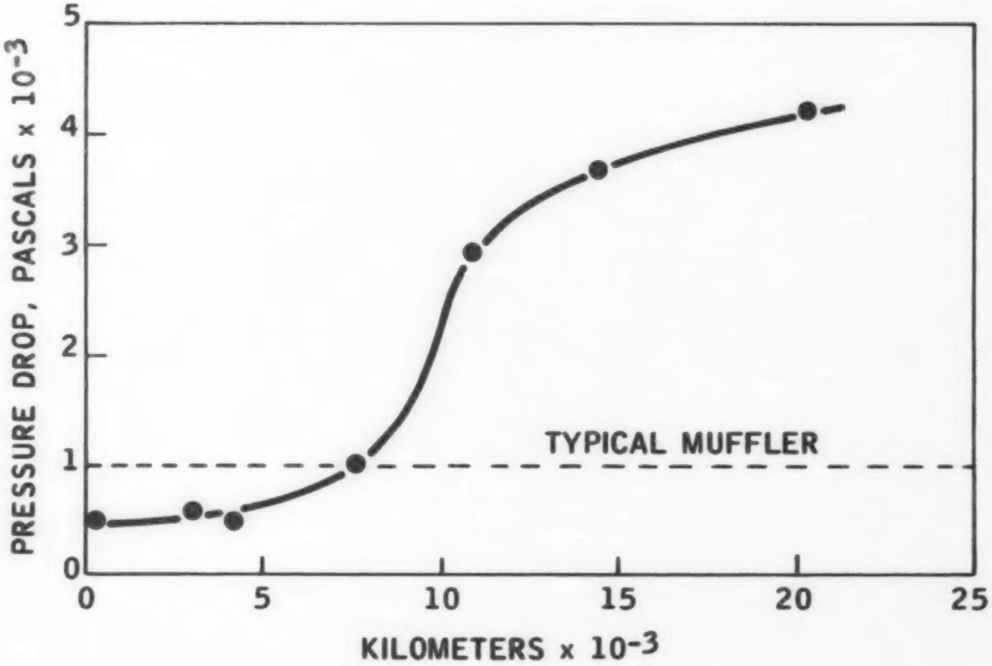


FIGURE VI - 4

PRESSURE DROP AT 64 KM/H—RINGS



areas of improvement with pellets should be available, however. If the composition is changed to lower the reactivity towards SO_2, then the rate of sulfation will be limited to that due to $SO_4^=$ pick-up only. This will result in a slower build-up of pressure drop and increased capacity for $SO_4^=$. Laboratory tests have indicated that the omission of Na_2O can reduce SO_2 pick-up, and this lead will be followed up with vehicle tests. In addition, to the extent accumulation of fine particles in the bed due to powdering of the pellets has increased the pressure drop, this can be minimized by learning how to make harder pellets.

The ring test showed that pressure drop can be lowered significantly, but initial efficiency and also capacity suffered. However, the first ring test reported here was carried out with a particle geometry chosen on the basis of die availability, rather than optimization of such factors as flow characteristics and surface to volume ratio. Therefore, further work with rings and other shapes, such as saddles, should result in further improvements. Improved canister geometry may also prove useful.

VI.4 Laboratory Screening of Sulfate Sorbents

VI.4.1 Experimental Procedure

Laboratory testing of sulfate sorbent candidates was carried out in a bench top reactor, illustrated in Figure VI-5. The sorbent, generally in the form of granules or approximately 3 mm pellets, was contained in a Vycor reactor, about 25 mm in diameter, mounted vertically in a tube furnace. Test temperatures were mostly 480°C, although some tests were run at 370°C. The constituents of the synthetic exhaust gas were blended through a bank of rotometers, to give the composition shown in Appendix Table E-22. The only exceptions were H_2O and SO_3 vapor, which were added by passing the heated gas through a 0.005 normal solution of H_2SO_4. No H_2, CO or HC was added to the gas stream, even though provision was made for them, since these components would be present in very small quantities in a real, post-catalyst exhaust gas, and should have no effect on sorbent activity. Thermocouples were mounted adjacent to the sorbent bed, whose volume was about 13 cm^3, to allow control and recording of the bed temperature.

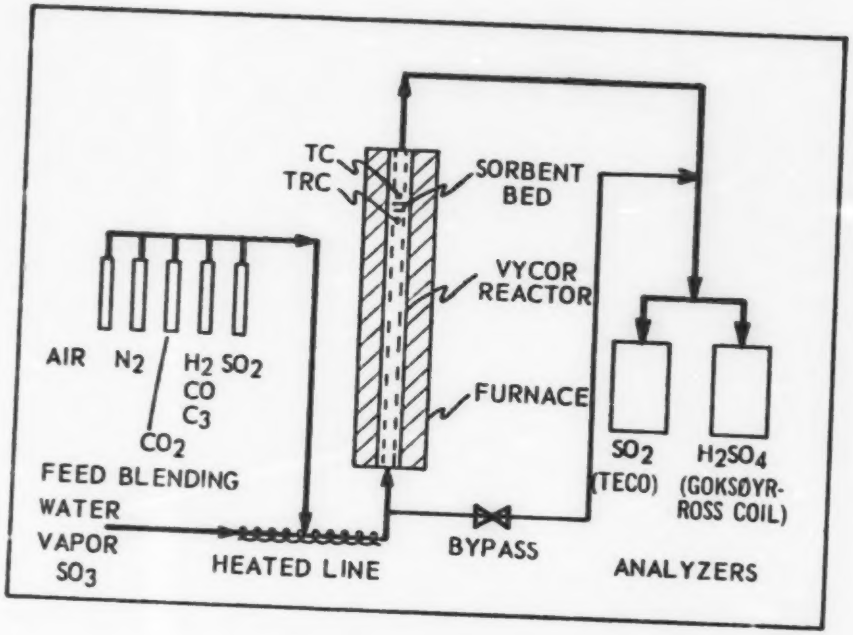
Analysis of the gas stream for SO_2 and SO_3 was made, before or after the sorbent bed, by means of a TECO UV fluorescence instrument and the Goksøyr-Ross coil. Both methods are described in Appendix B.

VI.4.2 Experimental Results

In addition to the benchmark material, a number of other possible sorbent materials have been screened. The primary purpose of this search was to find sorbents as active as the benchmark for sulfate pick-up, but

FIGURE VI - 5

APPARATUS FOR LABORATORY SCREENING OF SORBENTS


TC
TRC
SORBENT BED
VYCOR REACTOR
FURNACE
AIR
N_2
H_2 SO_2
CO
C_3
CO_2
FEED BLENDING
WATER VAPOR
SO_3
HEATED LINE
BYPASS
SO_2 (TECO)
H_2SO_4 (GOKSØYR-ROSS COIL)
ANALYZERS

(THE BYPASS IS LOCATED AFTER THE WATER VAPOR + SO_3 ARE ADDED.)

less active towards SO_2. Samples based on Ca, Al, Ba, Zr, Mg, Zn, and Mn have been studied. In some cases, commercial samples have been available in the proper size range and were tested as received. In other cases, the sorbents were prepared in house. In some cases, this required preparation of the powders, followed by pelleting, or if not suitable for pelleting, granulation and sieving. In others, suitable compounds were available for pelleting, if possible, or granulation and sieving if not. Appendix Table E-22 shows all of the materials tested, in what form and weight, for how long, and their activity towards sulfate and SO_2.

VI.4.2.1 Benchmark Sorbent

All of these experimental sorbents were compared to the benchmark material. The latter was tested at intervals in the laboratory reactor to insure that the equipment was functioning properly. As shown in Appendix Table E-22, all tests with this material showed complete or nearly complete sulfate pick-up, even out to 8.4 hours of exposure and a lower temperature of 370°C. Sorption of SO_2 was as high as 93% after 1-2 hours exposure, but fell to 79% after about 4 hours, at 370°C, and 35% after eight hours, at 370°C. The pellets used for these tests were made by the procedures described in Sections VI.2.2.1.1 and VI.2.2.1.2.

VI.4.2.2 Other Calcium Sorbents

Other calcium-based sorbents tested in this program included an 80 CaO/20 SiO_2 material, prepared in an analogous manner to the benchmark; a commercially available calcium silicate powder known as Micro-Cel, used for removing acidic components from organic liquids; commercial calcium carbonate chips, identical to those used in the vehicle durability test described in Section VI.2.3; and pellets formed from $Ca(OH)_2$, using an aluminum stearate binder, which dehydrated to CaO during calcination of the pellets. Except for the $CaCO_3$ chips, all of these calcium-based sorbents initially showed 100% efficiency for sulfate removal. The $CaCO_3$ had only about 75% efficiency after 1.3 hours, which fell to 50% after 3.7 hours. Of the other materials, the 80 CaO/20 SiO_2 and Micro-Cel pellets were tested for only 2.5 and 3.5 hours respectively, showing little or no activity loss. The CaO-binder sample, tested only at 370°C, fell from 100% removal at 3.2 hours to only 67% at 4.6 hours. The CaO-binder and $CaCO_3$ samples, therefore, have less capacity than the benchmark, but no conclusions can be drawn about the 80 CaO/20 SiO_2 and Micro-Cel materials. The SO_2 pick-up efficiency of all four of these calcium-based sorbents was much lower than for the benchmark, with the best, the CaO-binder combination, showing only 33% at 1 hour and falling to 12% after 4.6 hours.

The $CaCO_3$ material was tested in the form of chips, because $CaCO_3$ powder was too hard to form into pellets. The other three materials could be pelleted, but the resulting particles, while strong enough for laboratory reactor screening, were much weaker than the benchmark and would not have been suitable for vehicle testing. Thus, although good sulfate pick-up and proper selectivity towards SO_2 has been shown by calcium-based materials, none, except for the benchmark, are yet suitable for vehicle testing.

Several interesting points are worth further discussion in connection with calcium systems. First, the physical properties of the sorbent seem to affect the sorption efficiency. Of the four systems just described, the hardest, $CaCO_3$, was the least active. It also had the least surface roughness. Chemical composition would not be expected to play a role (H_2SO_4 is a strong acid and should react equally well with CaO, $Ca(OH)_2$ and $CaCO_3$). It should also be noted that although most of the calcium sorbents retained good sulfate pick-up efficiency, none were very active towards SO_2, except for the benchmark, which was the only one to also contain Na_2O. It would appear then that in the absence of highly basic sodium, good selectivity between sulfate and SO_2 pick-up can be achieved. This effect will also be seen with the magnesium sorbents described in the next section.

VI.4.2.3 Magnesium Sorbents

Four versions of magnesium-based sorbents were tested in the laboratory. The first was pure $Mg(OH)_2$, which was pelleted and then calcined. The resulting pellets were soft, but strong enough for laboratory evaluation. The second material consisted of spheres of magnesite, a naturally occurring $MgCO_3$. This was calcined to MgO, retaining its physical strength in the process. Third, commercially available pellets of MgO (Harshaw Chemical Company), were tested as received. Finally, a magnesium analog to the calcium benchmark material described in Section VI.4.2.1 was prepared in a similar manner.

All four of these magnesium-based sorbents initially showed complete removal of sulfate. Only the one containing Na_2O picked up any SO_2, again confirming the effect of basic sodium compounds. The Harshaw MgO pellets began to lose activity between the first and second hours, falling to about 75% at 2.7 hours and 17% at 4.2 hours. The other three did not show any loss, over total test periods ranging from 2.2 to 7.4 hours. The calcined magnesite maintained this activity even when the temperature was lowered to 370°C.

VI.4.2.4 Alumina Sorbents

Three different alumina samples were also tested. Two commercially available pellets, from Norton and Matheson, Coleman and Bell, were run. The latter was a high surface area, activated form. In addition, a section of honeycomb substrate, with a high surface area alumina washcoat, was also run. All three showed very poor activity for sulfate pick-up, and essentially none for SO_2.

VI.4.2.5 Other Sorbents

Several other sorbent materials were also tested. These were the oxides of Ba, Zr, Zn and Mn. Granules of BaO were a total failure, hydrating rapidly to $Ba(OH)_2$ and dissolving. Pellets of ZrO_2 were initially active for sulfate, but showed lower capacity than the benchmark. Starting from 100% efficiency after 1.3 hours only 84% pick-up was obtained at 4 hours. The temperature was lowered to 370°C, and activity at 5.1 hours was 73% and 12% at 8.8 hours. No SO_2 pick-up was observed. Zinc oxide extrudates showed good activity for 4.5 hours, initially at 480 °C, dropped to 82% at 3.9 hours, recovered to 100% at 4.5 hours and 370°C, but fell to 58% at 8.7 hours and 370°C. Little, if any SO_2 sorption was found. Finally, small MnO_2 granules were completely effective for sulfate removal for 2.7 hours, but fell to 82% at 3.9 hours. A relatively large amount of SO_2 was also picked up, 55% at 1.2 hours and 21% at 3.9 hours.

VI.4.3 Conclusions From Laboratory Screening Program

In addition to the previously identified benchmark sorbent, a number of other materials have been identified which show laboratory effectiveness for sulfate removal. Of these, some also offer an advantage over the benchmark sorbent in terms of a lower reactivity towards SO_2. These include the pelleted Ca-containing sorbents, the two calcined MgO samples, ZrO_2, ZnO, and MnO_2. Of these, only the Ca-based sorbents satisfy the criterion of having a water insoluble sulfate. Although a vehicle test would be necessary to determine with certainty whether or not a water soluble sulfate can be tolerated in a trap, we believe the next phase of testing should be restricted to calcium sorbents.

The prime difficulty encountered with the promising sodium-free calcium sorbents is an inability to form pellets strong enough to withstand vehicle testing. The ability of the benchmark material to be so fabricated indicates that Na_2O is acting as a binding agent. The problem then is to find a combination of other binding agents and preparation techniques which will allow the fabrication of strong pellets. In turn, this would allow vehicle testing of calcium sorbents which offer the promise of good selectivity between sulfate and SO_2.

VI.5 Effect of Space Velocity

In addition to the screening runs conducted at a space velocity of 100 000 v/v/hr, described in Section VI.4, several of the more active materials were also run at 150 000 v/v/hr, all at 480°C. This was done to provide some feel for the possibility of using smaller vehicle reactors, should underfloor space considerations require such a step. Samples of the benchmark, MgO (calcined magnesite) and ZnO which had been previously tested at 100 000 v/v/hr were kept on stream at the higher gas flow rate. All other conditions of gas composition and bed volume were maintained constant. A fresh charge of benchmark sorbent was also tested.

As shown in Appendix Table E-23, the previously used benchmark sorbent, which had seen 8.4 hours at the lower space velocity, maintained its high efficiency for sulfate trapping even after an additional 6.1 hours at the higher space velocity. At the end of the total of 14.5 hours, sulfate pick-up was still 100% and SO_2 pick-up 20%. The MgO sample, which had been tested for 7.4 hours at 100 000 v/v/hr, showed a sharp fall in sulfate efficiency after an additional 1.3 hours at the higher space velocity and was down to 40% after a total of 11.6 hours. Surprisingly, a small amount of SO_2 pick-up was seen at the higher space velocity, where none had been noted previously. The ZnO sample showed an anomalous result. After being exposed to feed gas for 8.2 hours at 100 000 v/v/hr, it showed only 50% sulfate sorption after about one hour at the higher space velocity. However, 2.5 hours later, still at 150 000 v/v/hr, sorption efficiency rose back to 100%. We have no explanation for this result. Finally, a fresh charge of benchmark sorbent was run for 4.2 hours at 150 000 v/v/hr, and showed an initial efficiency for sulfate of 100%, and 97% at the end. Pick-up of SO_2 was in the 70-80% range initially, and about 50% at 4.2 hours. The sulfate values are comparable to those at 100 000 v/v/hr, but the SO_2 pick-up rates are considerably lower.

Several sorbents were also tested at 50 000 v/v/hr. These were the benchmark, calcined magnesite and CaO. The benchmark material, after 4.2 hours at 150 000 v/v/hr. was exposed for an additional 10 hours at 50 000 v/v/hr. It showed complete sulfate pick-up over this interval, and an SO_2 sorption rate somewhat better than that seen at the highest space velocity. The calcined magnesite, after 11.6 hours at the two higher space velocities, was run for an additional 4.4 hours at 50 000 v/v/hr. Improved sulfate sorption was obtained. For example, at the 11.6 hour mark and 150 000 v/v/hr, only 40% trapping efficiency was noted, but at 16 hours and the lowest space velocity, this had risen to 64%. No improvement in SO_2 sorption with decreased space velocity was noted. The CaO sample had previously been run only at 370°C and 100 000 v/v/hr, falling to 67% sulfate efficiency at 4.6 hours. At the more favorable 480°C and 50 000 v/v/hr, however, 88% efficiency was obtained even after 8.9 hours total exposure. A higher level of SO_2 pick-up was also found.

Finally, fresh samples of the benchmark, calcined magnesite and MnO_2 sorbents were tested under the least favorable combination of conditions, high space velocity, 150 000, and low temperature, 370°C. As seen in Appendix Table E-23, all showed good initial activity for sulfate sorption, but lost this more rapidly than at higher temperatures and/or lower space velocities. The benchmark and MnO_2 samples also showed reduced SO_2 pick-up activity. The calcined magnesite exhibited the same zero efficiency for SO_2 as at the other operating conditions.

VI.6 Activated Charcoal for Sulfate Removal from Exhaust Gas

During the course of this contract, discussions were held with the Westvaco Corporation to determine if activated charcoal would be useful in a sulfate trap. The primary mechanism by which sulfate would be removed was expected to be reduction of SO_3 to SO_2 by reaction with carbon. A secondary mode could be the sorption of sulfate by the carbon. As a result of these discussions, a brief experimental program was conducted by Westvaco at their Charleston Research Center, North Charleston, S.C. Their report of this work is presented in full in Appendix Section D.2.

Briefly, Westvaco tested, in a laboratory reactor, the ability of activated carbon granules to remove sulfate from various simulated exhaust gas mixtures as a function of temperature, space velocity and granule size. It was found that at temperatures of about 315°C, almost complete conversion of SO_3 to SO_2 occurred using a fine (12 x 30 mesh) carbon bed and a space velocity as high as 60 000 V/V/ hr. However, conversion fell off rapidly as granule size increased or temperature was lowered. At the lower temperature the non-converted sulfate appeared to be sorbed in the carbon, and could be released as SO_2 upon heating to 315°C. Sorption efficiency also was adversely affected by increased mesh size and space velocity.

In addition to reactivity towards SO_3, the activated carbon could be expected to react with other oxidants in the exhaust, such as O_2, H_2O, and NO_x. A series of runs was also made therefore to determine the rates of these undesirable side reactions. It was found that, in addition to SO_3, O_2 and H_2O do react with the carbon to a significant extent at the 315°C temperature necessary to achieve good sulfate conversion. Various combinations of the three gaseous reactants, O_2, H_2O and SO_3 showed carbon burn-off rates 2-5 times greater than that due to SO_3 alone. Nitric oxide did not appear to react. At 370°C the burn-off rate increased by a factor of 7-10. Several runs were made with a carbon specially modified to minimize burn-off, and it was found to cut burn-off rate in half without apparently harming the SO_3 reaction rate.

As a result of this work, it has been concluded that it would be extremely difficult, if not impossible, to utilize activated carbon in a practical sulfate trap. The principal drawback is the rapid reaction which will occur at the usual vehicle-mounted trap temperatures, around 370°C, between oxidants such as O_2 and H_2O and the carbon. This burn-off will result in rapid depletion of the bed material, as well as possibly leading to CO formation and a fire hazard. Although there may be a narrow temperature region in which acceptable rates of sulfate reaction and burn-off can be compromised, a complex temperature control system would be necessary to maintain it over the full range of driving conditions.

VII. References

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6. M. Beltzer, et al., "The Conversion of SO_2 Over Automotive Oxidation Catalysts" SAE Paper 750095, February, 1975.

7. B. J. Kraus, et al. "Critical Factors Affecting Sulfate Emissions" SAE Paper to be presented February, 1976.

8. Letter to Senator Jennings Randolph from D. G. Levine, Exxon Research and Engineering Company, November 16, 1973.

Appendix A

Task I - Literature Search

A.1 Introduction

This literature search was conducted to bring together and examine the literature pertaining to the fate of sulfur oxides in automotive exhaust systems. Currently available gasoline averages about 300 ppm sulfur in the form of organic sulfur compounds. During the combustion process, gasoline sulfur is oxidized to sulfur dioxide. In non-catalyst vehicles, this sulfur dioxide is emitted to the atmosphere. In vehicles equipped with oxidation catalysts for control of carbon monoxide and hydrocarbon emissions, further oxidation to sulfur trioxide, SO_3, takes place. This SO_3 can then combine with water, forming sulfuric acid. The literature was reviewed to investigate the thermodynamic potential and kinetics of forming the trioxide and to examine the fate of both oxides in the exhaust system. Since sulfuric acid emissions may be deleterious, the literature pertaining to removal of sulfur oxides from gaseous streams was reviewed. Stress was placed on the use of metal-oxide sorbents for this purpose.

To cover these subjects, the body of this report is divided into four sections. The first section details the thermodynamics of sulfur trioxide formation, reaction with water, and condensation. The second section examines possible reaction with materials in the exhaust gas or system. The third system reviews the catalytic oxidation of sulfur dioxide on platinum catalysts. The last section examines possible means of removing sulfur trioxide from the exhaust stream.

A.2 Summary and Conclusions

A.2.1 Thermodynamics of Sulfuric Acid Production

1. At typical oxidation catalyst temperatures, conversions of sulfur dioxide to sulfur trioxide greater than 50% are thermodynamically possible.

2. The equilibrium conversion is strongly dependent upon oxygen concentration. At temperatures above 400°C, decreasing the oxygen concentration decreases the equilibrium conversion, suggesting a possible control strategy.

3. Thermodynamics and kinetics show that exhaust sulfur trioxide may hydrate to gaseous sulfuric acid within the vehicle's exhaust system, depending upon driving mode.

4. Thermodynamics show that the gaseous sulfuric acid will begin to condense at about 150°C which is below the temperature at the tailpipe exit for all driving modes except startup.

A.2.2 Reaction of Sulfur Dioxide and Trioxide with Exhaust Gas Constituents and Exhaust System Components

1. Thermodynamics shows that ammonia will reduce sulfur trioxide to the dioxide. However, exhaust ammonia will be oxidized over the oxidation catalyst before reaction can take place.
2. The formation of ammonium sulfate is favorable only below 225°C.
3. Thermodynamics shows that the reduction of both sulfur oxides by carbon monoxide is favorable.
4. Reaction of both oxides with the iron oxide surfaces of the exhaust system is favorable below 425°C.
5. Reaction of sulfur trioxide with the aluminum oxide catalyst substrate is possible below 425°C. The presence of carbon monoxide may lower this temperature by about 50°C.

A.2.3 Automotive Catalysis of Sulfur Dioxide

1. The rate limiting step in the catalytic oxidation of sulfur dioxide is the surface reaction between adsorbed oxygen and adsorbed sulfur dioxide.
2. The following rate equation appears to represent best the available experimental data for industrial catalysis and should be valid for automotive catalysis

$$\text{rate} = \frac{k_1 \left(P_{SO_2} P_{O_2}^{1/2} - \frac{P_{SO_3}}{K^e}\right)}{\left(1 + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{SO_3} P_{SO_3}\right)^2}$$

Where k_1 is the rate constant, subscripted P's are the partial pressures of the compounds in the subscripts, K^e is the equilibrium constant of the oxidation reaction, and the subscripted K's are the absorption equilibrium constants for the compounds in the subscripts.

This equation is in accord with the above rate limiting mechanism. This equation also indicates a possible control strategy of limiting the amount of oxygen over the catalyst.

3. The automotive catalysis literature is limited. In addition, the data are confounded by many experimental problems, notably the storage/release phenomenon. In general, this literature says that more sulfur trioxide is formed over catalysts than with non-catalyst vehicles but good quantitative data are lacking.

A.2.4 Sulfate Traps

1. The most promising means of removing sulfur trioxide from the exhaust stream is to react it with a basic metal oxide.

2. Based on a selection criterion consisting of seven requirements, the most promising sorbent material is calcium oxide. Other less promising but still attractive sorbents are the oxides of magnesium, manganese, and aluminum.

A.3 Thermodynamics of Automotive Sulfuric Acid Production

In assessing the production and fate of sulfuric acid within a vehicle's engine or exhaust system, there are three basic reactions which must be considered. These reactions are: the reaction of sulfur dioxide with oxygen to form sulfur trioxide, the hydration of the sulfur trioxide to gaseous sulfuric acid, and the condensation of the gaseous acid to produce a finely dispersed aerosol. The first reaction is important as it shows that the formation of substantial amounts of sulfur trioxide is thermodynamically possible at typical automotive catalyst temperatures. The second and third reactions are important since they define the state, sulfur trioxide, gaseous sulfuric acid, or condensed sulfuric acid aerosol, in which the sulfur trioxide will exist in the exhaust system. This is important from the point of view of controlling the potential emissions within the exhaust system. Hydration of the trioxide is possible during some driving modes. Condensation, however, is unfavorable except possible at start-up and idle.

A.3.1 Thermodynamics of Sulfur Trioxide Production

The reaction of sulfur dioxide with oxygen can proceed either homogeneously or catalytically. The homogeneous reaction is extremely slow (14) and would be negligible considering the very small residence times within the vehicle, typically on the order of a few seconds. In the presence of oxides of nitrogen, the rate of sulfur dioxide oxidation is increased markedly. A calculation using the rate-constant data from Duecker and West (14) shows that under high NO conditions, such as high speed or load, the conversion of sulfur dioxide to the trioxide would be $\sim$1.0%. Since the reaction rate depends on the square of the NO partial pressure, the conversion would be much less under low NO conditions. The heterogeneous catalysis of this reaction will be discussed later.

No matter how rapid the reaction rate, the maximum conversion will be limited by thermodynamic equilibrium. Table A-1 (48) lists the free energies and equilibrium constants for the reaction as written

$$SO_2(g) + 1/2\ O_2(g) \rightleftharpoons SO_3(g). \qquad (1)$$

The equilibrium constant for this reaction is

$$K^e = \frac{\left(P_{SO_3}\right)}{\left(P_{O_2}\right)^{1/2}\left(P_{SO_2}\right)} , \qquad (2)$$

where P indicates component partial pressure in atmospheres. Figure A-1 shows the effect of temperature on the conversion for typical exhaust gas compositions. Lines of different oxygen concentration are shown to illustrate the effect of differing air injection rates upstream of an automotive oxidation catalyst. As this figure illustrates, increasing the oxygen content of the exhaust increases the maximum possible conversion to sulfur trioxide. In the region of typical oxidation catalyst temperatures, 500 to 650°C, the maximum possible conversion is between 90 and 50% when using an air pump supplying 5% oxygen. Assuming that equilibrium controls the oxidation of sulfur dioxide, operation of the vehicle at stoichiometric or slightly lean air-to-fuel ratios, either by careful carburetion or by using a three-way catalyst system, the production of sulfur trioxide

TABLE A-1

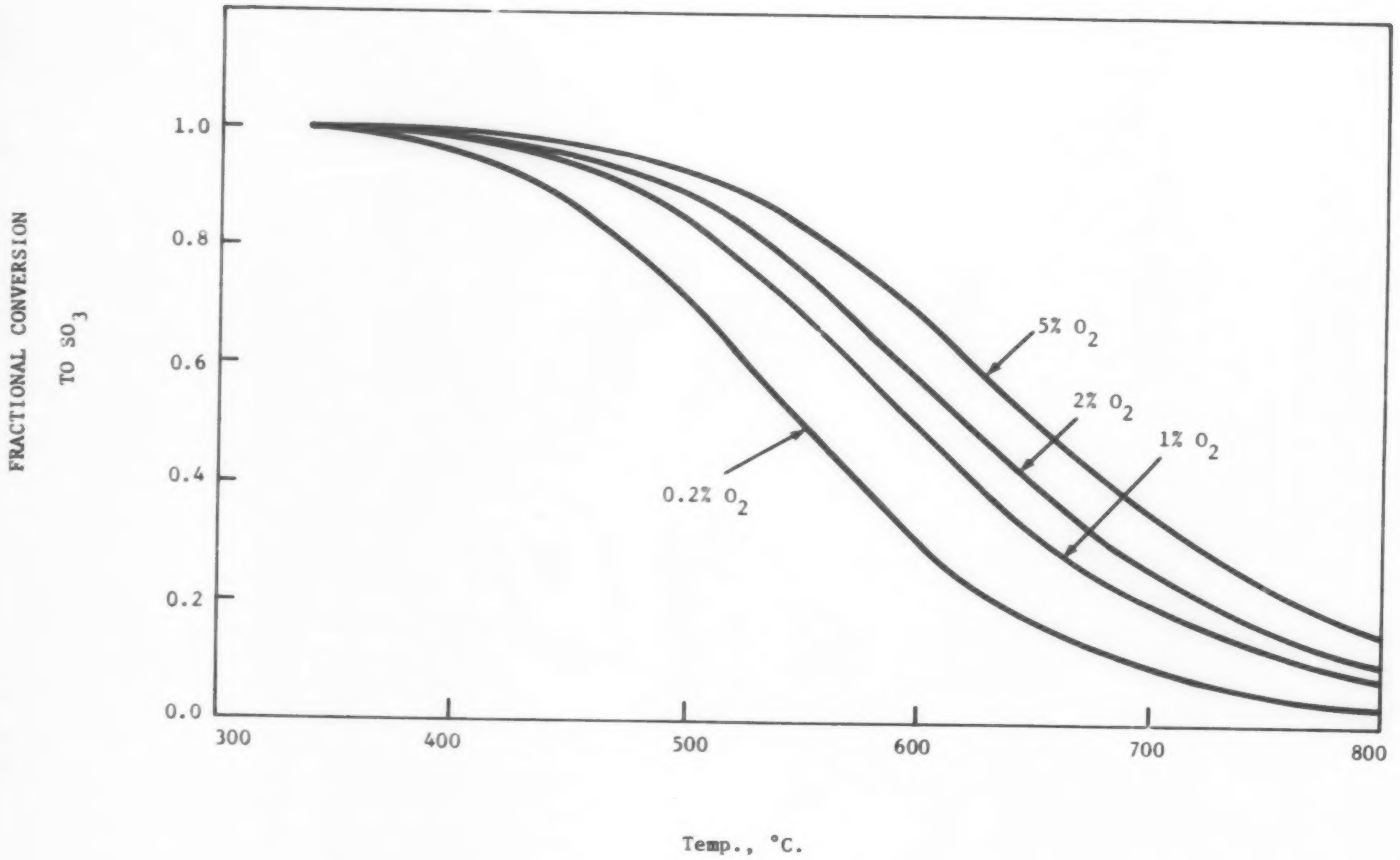
Equilibrium Constants for the Oxidation of Sulfur Dioxide to Sulfur Trioxide

Temperature (°K)	Free Energy of Reaction (K cal/mole)	Equilibrium Constant (atm $^{-1/2}$)
300	-16906.50	2.069×10^{12}
350	-15775.99	7.088×10^{9}
400	-14649.01	1.008×10^{8}
450	-13520.27	3.682×10^{6}
500	-12389.19	2.600×10^{5}
550	-11257.38	2.972×10^{4}
600	-10127.01	4.892×10^{3}
650	- 8999.82	1.061×10^{3}
700	- 7876.73	2.878×10^{2}
750	- 6757.71	9.313×10^{1}
800	- 5642.04	3.477×10^{1}
850	- 4528.59	1.460×10^{1}
900	- 3416.23	6.754
950	- 2304.12	3.389
1000	- 1192.02	1.822
1050	- 80.38	1.039
1100	+ 1029.68	6.244×10^{-1}

Figure A-1

Equilibrium Conversion

$SO_2(g)+1/2\ O_2(g) = SO_3(g)$



could be reduced. For instance, operation at 0.2% oxygen instead of 5% could reduce the conversion by 25 to 65% over the typical oxidation-catalyst temperature range. However, at the lower temperatures, absolute conversions could still be as high as 70% at the 0.2% level. Therefore, from an equilibrium standpoint, reduction of the oxygen content of the exhaust could result in lowering sulfur trioxide production. However, absolute control would not be feasible. The kinetics of this reaction will be discussed in the Automotive Catalysis section.

A.3.2 Thermodynamics of Sulfur Trioxide Hydration

As the SO_3 produced by the engine or over an oxidation catalyst proceeds through the exhaust system, it is cooled significantly. As the temperature drops, the hydration of sulfur trioxide to gaseous sulfuric acid becomes more favorable as shown in Figure A-2, where the fraction of sulfur trioxide hydrated to gaseous sulfuric acid is given as a function of temperature. This plot was generated using equilibrium constants calculated from Eqn. (17) of Gmetro and Vermeulen (20). Hydration begins at about 450°C and is complete at about 200°C. Typical tailpipe exit temperatures range from ∿200 to over 500°C (our measurements, 24) for conditions from idle to extended high speed driving. Thus, it is possible for sulfur trioxide to either survive throughout the exhaust system or to be completely hydrated depending upon the driving mode. Gillespie and Johnstone (19) in studying sulfuric acid formation found that dry sulfur trioxide would form an aerosol instantaneously upon contact with moist air. These results imply that the hydration reaction is extremely rapid and would be controlled by equilibrium in an exhaust gas environment.

A.3.3 Thermodynamics of Sulfuric Acid Condensation

The dew point of gaseous sulfuric was experimentally determined and compared with calculated thermodynamic values by Lisle and Sensenbaugh (39). They found excellent agreement. The calculated dew point as a function of temperature is shown in Figure A-3. More recently, Verhoff and Banchero (56) have reviewed the literature concerning sulfuric acid dew points and correlated the data which they felt were accurate. The resulting least squares correlation is shown in Figure A-3 for a water content of 12%. As this figure shows, both curves predict dew points within a few degrees of each other in the range applicable to exhaust sulfuric acid levels.

A typical vehicle operating on an average fuel of 300 ppm sulfur would produce exhaust containing approximately 10 ppm H_2SO_4 assuming 50% conversion of sulfur dioxide to trioxide. At this concentration, condensation would begin at ∿133°C which is below the exhaust temperature at the tailpipe exit. The rate of condensation, as pointed out previously, is very rapid, therefore, should the exhaust temperature

Figure A-2

Equilibrium Conversion

$SO_3(g) + H_2O(g) == H_2SC_4(g)$

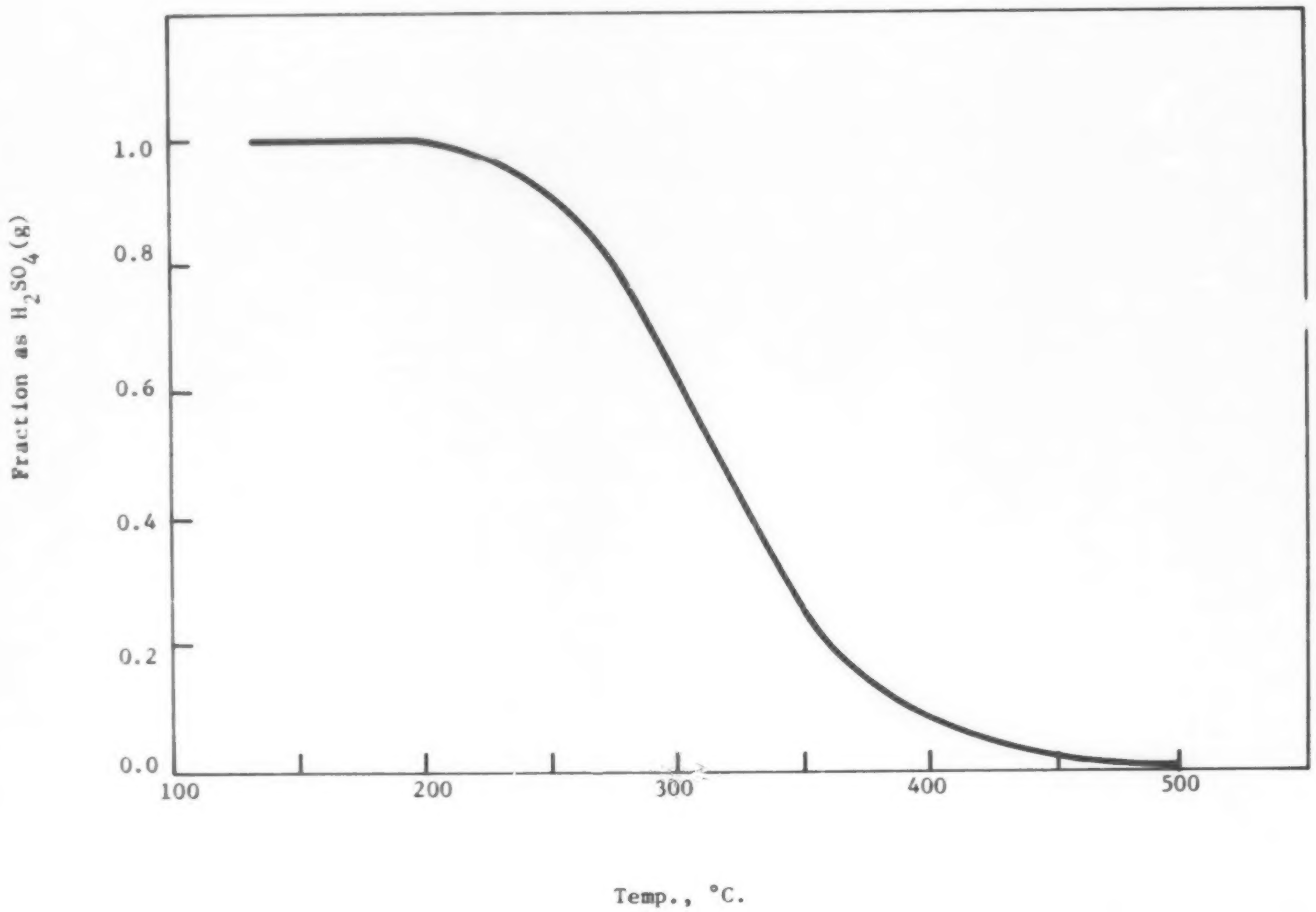
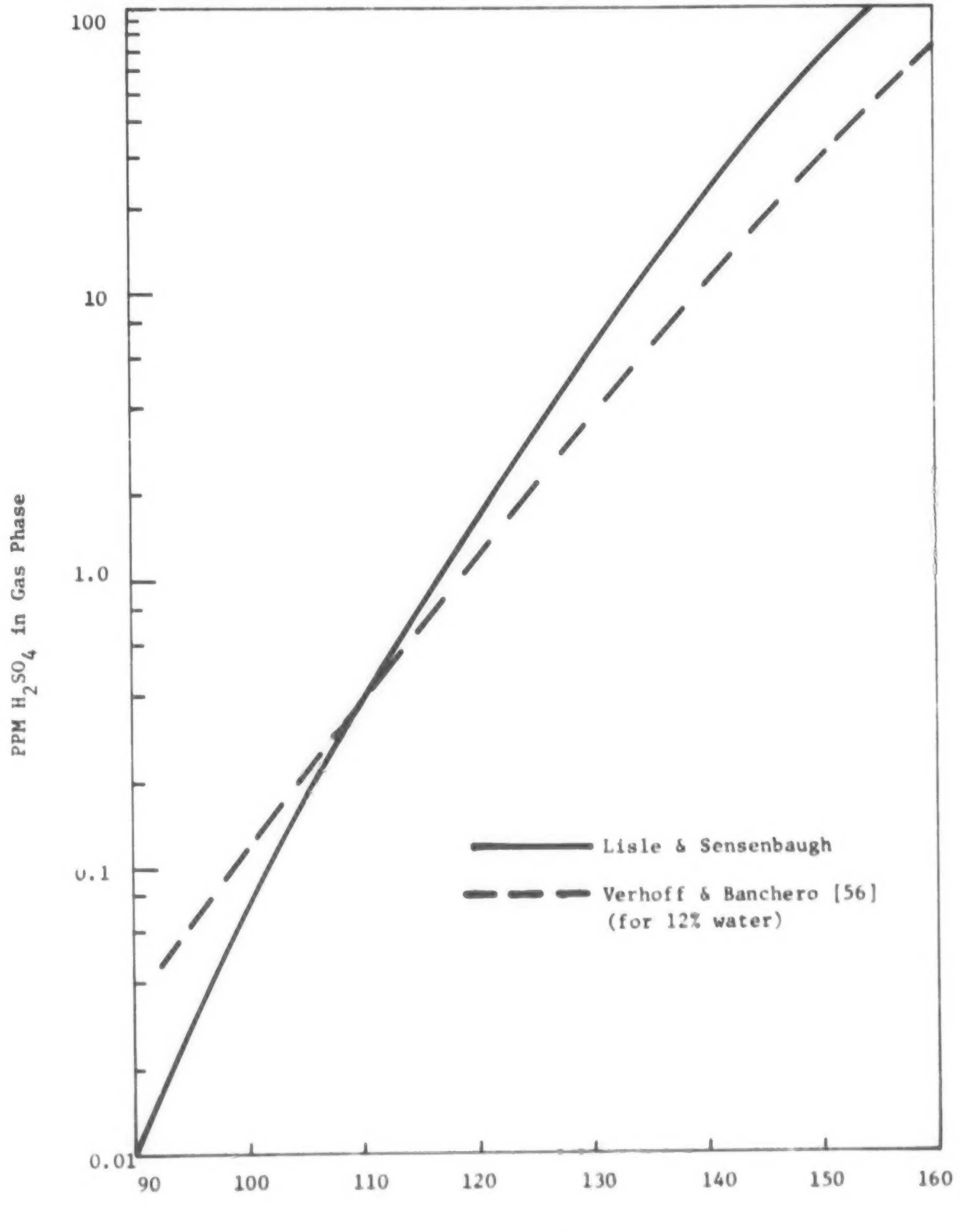


Figure A-3

Dew Point of $H_2SO_4(g)$



drop below 133°C, condensation of the gaseous sulfuric acid would immediately occur in the tailpipe. However, for the majority of driving situations, the sulfuric acid would exit the tailpipe in the vapor rather than the condensed state.

A.4 Reaction of Sulfur Dioxide and Trioxide with Exhaust Gas Constituents and Exhaust System Components

There are several exhaust gas constituents and system materials with which the sulfur oxides can react. The two main exhaust gas constituents capable of reaction with sulfur dioxide and sulfur trioxide are ammonia and carbon monoxide, both of which are more basic than the sulfur oxides. The pertinent reactions are:

$$2NH_3 + SO_3 + H_2O \rightleftharpoons (NH_4)_2\ SO_4 \qquad (3)$$

$$2NH_3 + 3SO_3 \rightleftharpoons N_2 + 3H_2O + 3SO_2 \qquad (4)$$

$$SO_3 + CO \rightleftharpoons CO_2 + SO_2 \qquad (5)$$

$$2SO_2 + 4CO \rightleftharpoons S_2 + 4CO_2 \qquad (6)$$

The first reaction is thermodynamically unfavorable at exhaust temperatures and, further, any ammonia would be oxidized over the oxidation catalyst before reaction with the trioxide could take place. The second reaction is also very unlikely due to the oxidation of the ammonia. The reduction reactions by carbon monoxide are both favorable but most likely limited due to kinetics. The reactions of both sulfur oxides with the iron or aluminum oxide catalyst support are favorable. The aluminum oxide can alternately form the sulfate and decompose as the catalyst temperature cycles during transient driving modes producing a sulfate storage/release phenomena.

A.4.1 Reaction of Ammonia with Sulfur Trioxide

The free energies and equilibrium constants for Reaction 3 are given as functions of temperature in Table A-3. The thermodynamic equilibrium constant, given by the relationship

$$Kp = \frac{1}{\left(P_{NH_3}\right)^2 \left(P_{H_2O}\right)\left(P_{SO_3}\right)^3}$$

for an exhaust gas containing 10 ppm NH_3, 12% H_2O, and 10 ppm SO_3 is 8.3×10^{15} atm^{-4}. Comparison of this value with the equilibrium constants in Table A-2 shows that the reaction is favorable only at temperatures below 225°C. Since the equilibrium constants are such a strong function of temperature, order of magnitude changes in the concentration of either ammonia or sulfur trioxide will not appreciably alter the temperature at which the reaction becomes thermodynamically favorable. Temperatures below 225°C occur in the exhaust only at the tailpipe exit and only during start up and some extended idle periods. Thus, the production of ammonium sulfate in the exhaust system would be possible only during these modes. Ammonium sulfate may, however, be formed after exiting the tailpipe in either the atmosphere or a particulate sampling apparatus. The thermodynamic favorability of this occurrence would depend simultaneously upon the cooling and dilution rates.

TABLE A-2

Free Energies and Equilibrium Constants for the Reaction of Ammonia and Sulfur Trioxide Forming Ammonium Sulfate (33)

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-4})
298	-63,830	6.18×10^{46}
400	-49,100	6.75×10^{26}
500	-34,900	1.80×10^{15}
600	-21,000	4.47×10^{7}
700	- 7,400	5.32
800	+ 5,800	2.60×10^{-2}

The possibility of ammonium sulfate production is most likely in catalyst-equipped vehicles where the potential of forming sulfur trioxide is greatest. However, in these vehicles, the oxidation of ammonia over the catalyst must be considered. The oxidation of ammonia over platinum to produce nitric oxide is a very important and well-known industrial reaction (15). The reaction is very rapid with almost complete oxidation.

TABLE A-3

Free Energies and Equilibrium Constants for the Reaction of Ammonia and Sulfur Trioxide to form Nitrogen, Water, and Sulfur Dioxide (33)

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-4})
298	-105,510	2.21×10^{77}
400	-114,100	2.22×10^{62}
500	-122,500	3.54×10^{53}
600	-131,000	5.26×10^{47}
700	-139,400	3.36×10^{43}
800	-147,700	2.25×10^{40}
900	-155,900	7.26×10^{37}
1000	-164,100	7.36×10^{35}

A.4.2 Reduction of Sulfur Trioxide by Ammonia

Reaction 4 illustrates a reaction mechanism whereby exhaust ammonia can be consumed. The equilibrium thermodynamics for this reaction are given in Table A-3. The extremely large equilibrium constants show that this reaction has the potential of almost complete removal of either the ammonia or the sulfur trioxide, whichever is initially present at lower concentration. Assuming that the reaction kinetics are sufficiently rapid, this reaction would then preclude the formation of ammonium sulfate.

Typical automotive exhaust without catalysts contains from one to six ppm ammonia depending upon driving mode with an average of 2.2 for a typical driving cycle (23). Our results with the dual-catalyst system show that an active automotive oxidation catalyst will readily oxidize ammonia resulting in tailpipe concentrations typically less than 1 ppm. Therefore, even at low exhaust temperatures where ammonium sulfate formation is thermodynamically favorable, only small amounts could be made. This agrees with Ford Motor Company's finding (17) that little or no ammonium sulfate or bisulfate is found in automotive particulate.

A.4.3 Reduction of Sulfur Trioxide by Carbon Monoxide

Reaction 5 is a second possible reaction which would lead to a reduction in sulfur trioxide emissions. The equilibrium thermodynamics for this reaction, as given in Table IV, were calculated from data presented in the JANAF Thermochemical Tables (20). The equilibrium constants indicate that, even for carbon monoxide concentrations in the ppm range, the reaction is favorable at exhaust gas concentrations. The extent of the reaction would, however, probably be limited by the reaction rate.

TABLE A-4

Free Energies and Equilibrium Constants for the Reduction of Sulfur Trioxide by Carbon Monoxide

Temp (°K)	Free Energy (Cal/mole)	Equilibrium Constant (dimensionless)
500	-44,870	4.11×10^{19}
600	-45,020	2.51×10^{16}
700	-45,160	1.26×10^{14}
800	-45,310	2.39×10^{12}
900	-45,450	1.09×10^{11}
1000	-46,670	1.59×10^{10}

A.4.4 Reduction of Sulfur Dioxide by Carbon Monoxide

The last possible reaction is the reduction of sulfur dioxide to elemental sulfur by reaction with carbon monoxide. The thermodynamic data calculated from the JANAF Tables (30) are presented in Table A-5. The equilibrium constant for this reaction is written as,

$$Kp = \frac{P_{CO_2}^{4}}{P_{CO}^{4}\ P_{SO_2}^{2}} \qquad (8)$$

In a pre-catalyst vehicle, typical exhaust concentrations would be $P_{CO_2} = 0.12$ atm, $P_{SO_2} = 2 \times 10^{-5}$ atm, and $P_{CO} = 0.01$ atm. At these levels, the reduction of sulfur dioxide by carbon monoxide would become favorable at temperatures below 600°C. In a catalyst vehicle the partial pressure of carbon monoxide would be typically less than 10^{-4} atm in which case the reaction would become favorable at temperatures less than 375°C. Hence, for both catalyst and non-catalyst vehicles, the reduction of sulfur dioxide to elemental sulfur is thermodynamically feasible within the exhaust system.

TABLE A-5

Free Energies and Equilibrium Constants for the Reduction of Sulfur Dioxide by Carbon Monoxide

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-2})
500	-73,390	1.21×10^{32}
600	-68,440	8.54×10^{24}
700	-63,560	7.01×10^{19}
800	-58,660	1.06×10^{16}
900	-53,800	1.16×10^{13}
1000	-48,540	4.07×10^{10}

A.4.5 Reaction of Sulfur Oxides With Iron

The most prevalent solid material with which sulfur oxides can react is the iron of the engine and exhaust system. Since the newer model cars and all future oxidation catalyst vehicles are operated net lean, either by carburetion or by air injection, the internal iron surfaces of the exhaust system will be oxidized. A typical iron-sulfur oxide reaction is the sulfation of ferric oxide by sulfur trioxide,

$$Fe_2O_3 + 3SO_3 \rightleftharpoons Fe_2\ (SO_4)_3. \qquad (9)$$

A similar type of reaction can also be written for sulfur dioxide where iron sulfite is the product. These types of reactions are industrially important in the corrosion of iron or steel surfaces in contact with flue or stack gases containing oxides of sulfur. In this vein, the sulfation of iron has been examined by several researchers (35, 36, 24). Warner and Ingraham (58, 59) have also investigated the reverse reaction in their studies on the processing of metallic ores.

These studies as well as thermodynamic calculations, show that the sulfation of ferric oxide by sulfur trioxide in the concentration range of catalyst vehicles becomes favorable at temperatures below 450°C. Table A-6 contains the pertinent thermodynamic data. Therefore, sulfation is possible over a large fraction of the exhaust system. Furthermore, there will be a zone in which the temperature will oscillate, as the driving mode changes, around the temperature at which the reaction is favorable. It is, therefore, possible for this zone to either pick up or release sulfur oxides depending upon the temperature and sulfur oxide concentration.

TABLE A-6

Free Energies and Equilibrium Constants for the Reaction of Sulfur Trioxide with Ferric Oxide

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-3})
500	-70,730	8.29×10^{30}
600	-57,790	1.13×10^{21}
700	-49,940	3.92×10^{15}
800	-32,170	6.15×10^{8}
900	-19,420	5.20×10^{4}
1000	- 6,720	2.94×10^{1}

Warner and Ingraham (59) allude to the mechanism of ferric sulfate decomposition. Their work with decomposition under atmospheres of varying sulfur dioxide and trioxide compositions indicates that the decomposition products are more likely to be sulfur dioxide and oxygen than sulfur trioxide.

Therefore, it is possible to store sulfate in the exhaust system by the reaction of sulfur trioxide with iron and then to release this stored sulfate as sulfur dioxide and oxygen.

The relative reaction rates of iron sulfation by sulfur dioxide and sulfur trioxide can be assessed from the work of Pechkovsky (44) and Krause, et al. (35). Pechkovsky studied the reaction of sulfur dioxide with various metal oxides in an oxidizing environment. He showed that sulfation of some metals, notably magnesium oxide, was very slow with only sulfur dioxide present. When a small amount of catalyst, such as ferric oxide, was added, the reaction proceeded much more rapidly, presumably due to the oxidation of sulfur dioxide to the trioxide which then reacted more readily. Krause, et al. (35), using a radioactive tracer technique, found sulfur trioxide to be on the order of 10^4 times more reactive on a molar basis than the dioxide.

A.4.6 Reactions of Sulfur Trioxide with Aluminum Oxide

Another material in the exhaust system of a catalyst-equipped vehicle with which sulfur trioxide can react is the aluminum oxide catalyst substrate via the reaction

$$Al_2O_3 + 3SO_3 \rightleftharpoons Al_2(SO_4)_3. \qquad (13)$$

The thermodynamic data for this reaction (33) are given in Table A-7 for gamma form of aluminum oxide. The equilibrium partial pressures for sulfur trioxide are also presented in this table. These data show that this reaction is favorable for typical sulfur trioxide exhaust gas compositions when the temperature is below 425°C. While no quantitive data are available on the kinetics of this reaction, qualitatively they are rapid enough to be significant as witnessed by the sulfate storage noted by several investigators (2, 18, 45).

TABLE A-7

Free Energies, Equilibrium Constants, and Equilibrium Partial Pressures for the Reaction of Sulfur Trioxide with Gamma Aluminum Oxide

Temp (°K)	Free Energy (cal/mole)	Equilibrium Constant (atm^{-3})	Equilibrium Partial Pressure of Sulfur Trioxide (atm)
298.16	111,000	2.34×10^{81}	7.53×10^{-28}
400	96,900	8.87×10^{52}	2.24×10^{-18}
500	83,200	2.34×10^{36}	7.53×10^{-13}
600	69,900	2.91×10^{25}	3.25×10^{-9}
700	56,700	5.05×10^{17}	1.26×10^{-6}
800	43,800	9.25×10^{11}	1.03×10^{-4}
900	30,900	3.19×10^{7}	3.15×10^{-3}
1000	18,200	9.50×10^{3}	4.72×10^{-2}

The release of this stored sulfur can also play an important part in automobile sulfate emissions. As the above reaction indicates, the aluminum sulfate can decompose back to the oxide with the release of sulfur trioxide. Such a release would become thermodynamically favorable above 420°C. Warner and Ingraham have examined the thermodynamics (58) and kinetics (59) of the decomposition of aluminum and ferric sulfates. As discussed above, they found that the rate of ferric sulfate decomposition was proportional to the sulfur dioxide driving force. That is to say that the decomposition favors the formation of sulfur dioxide rather than the trioxide. Although they did not investigate the mechanism of aluminum sulfate decomposition, by analogy with ferric sulfate decomposition, aluminum sulfate could decompose into oxygen and sulfur dioxide. Thus, it could be possible for sulfur trioxide formed on the catalyst to react with the substrate only to be released later at a higher temperature as sulfur dioxide. With this possibility, care must be exercised in designing and interpreting experiments examing the fate of gasoline sulfur over an oxidation catalyst.

Kelly (33) presents an alternate route for aluminum sulfate decomposition in the presence of carbon monoxide. The reaction is

$$Al_2(SO_4)_3 + 3CO \rightleftharpoons Al_2O_3 + 3SO_2 + 3CO_2. \qquad (11)$$

The equilibrium constant for this reaction, $K^{1/3} = P_{SO_2} P_{CO_2}/P_{CO}$ is on the order of 3×10^9 atm for all temperatures. Since this equilibrium constant is very large, the partial pressure of carbon monoxide must be extremely small before this reaction becomes unfavorable. Thus this reaction may provide a route for sulfate release. Kelley feels that the actual mechanism of this reaction is the decomposition of aluminum sulfate to sulfur trioxide which is subsequently reduced to sulfur dioxide by carbon monoxide. He feels that the addition of carbon monoxide may reduce the decomposition temperature of aluminum sulfate by about 50°C.

A.5 Automotive Catalysis of Sulfur Dioxide

The only oxidation catalysts presently envisioned for automotive application are platinum and platinum-alloy catalysts. This section will, therefore, be limited to these catalysts. The bulk of the literature covering platinum oxidation of sulfur dioxide pertains mainly to use in sulfuric acid plants and, to a much lesser extent, in flue gas sulfur dioxide control. In these applications, the sulfur dioxide concentrations are much higher, 5-8% and 1% respectively, than found in typical automotive exhaust, 20 ppm. Even though the exhaust concentration is orders of magnitude below the percent level, the kinetic mechanism of catalysis over platinum should be the same. This suggests that the rate equations would also be valid. The first part of this section will review this literature. The second part will review the more limited, recent literature dealing directly with the sulfur dioxide oxidation over automotive catalysts.

A.5.1 Platinum Catalysis: Industrial Application

The use of platinum as a catalyst in the oxidation of sulfur dioxide was first disclosed in a patent by Peregrine Phillips in 1831 (41). This discovery is considered the foundation of the contact process for manufacturing sulfuric acid.

It wasn't until the 1900's that quantitative data became available concerning the rate and the mechanism of the oxidation reaction over various forms of platinum. This began with the classic work of Knietsch (34) in 1901. Knietsch examined the effect of space velocity and inlet concentrations on the conversion of SO_2 as a function of catalyst temperature. The catalyst consisted of 0.5 gm. of platinum supported on 5 to 10 gms. of asbestos. The oxygen concentration was held constant at 10% and 7 - 20% SO_2 concentrations were examined over the temperature range of 300 to 900°C. For this range of variables, conversions of from 0 to 99% were obtained. At a given space velocity, the experimental conversion was low at 300°C. As the temperature was increased, the conversion increased, rapidly reaching a maximum in the temperature range of 400-500°C depending upon space velocity. Maximum conversions were in the range of 70 to 99% again depending upon space velocity. The lower space velocities peaked at lower temperatures and at greater conversions. As the temperature was increased further, the conversions decreased paralleling equilibrium with the lower space velocities nearer equilibrium. The limited data at the higher SO_2 level (20% instead of 7%) showed a decrease in conversion at identical temperature and space velocity. From these data, Knietsch deduced that the reaction rate was proportional to the concentrations of sulfur dioxide and oxygen (61) and is independent of the concentration of sulfur trioxide. The accuracy of these data have since been questioned due to Knietsch's poor temperature control and large conversions.

In another classical study of heterogeneous catalysis, Bodenstein and Fink (6,7) investigated the oxidation of SO_2 over a platinum gauze of 0.06 mm diameter wire. This study, conducted over the experimental temperature range of 150-250°C, produced a reaction rate which is proportional to the first power of the sulfur dioxide concentration and inversely proportional to the square root of the sulfur trioxide concentration for the case where $C_{SO_2}/C_{O_2} = 3$. Where this ratio is greater than 3, the reaction rate is proportional to the first power of the oxygen concentration and inversely proportional to the square root of the sulfur trioxide concentration. The usefulness of these rate equations is, however, somewhat limited due to the very low temperatures investigated.

Lewis and Ries (37, 38), objecting to the poor control of experimental conditions by Knietsch and to Bodenstein's low temperature range, obtained catalytic data under carefully controlled conditions approximating actual contact plant operations. Their kinetic experiments were designed and conducted so as to approximate a differential reactor, that is, a reactor in which the conversion is allowed to change only to a small extent. Thus, the reaction is taking place throughout the reactor with approximately the same reactant and product concentrations. In addition, the temperature does not change due to reaction exo- or endothermicity since conversions are differential. This is the classically accepted method for obtaining accurate kinetic data.

Lewis and Ries performed three separate series of tests. In the first series the effect of inlet sulfur dioxide concentration was examined by varying the amount of sulfur dioxide in an air-sulfur dioxide feed. In the second series, the amount of oxygen was varied by dilution of the air-sulfur dioxide feed with nitrogen. The final series examined the effect of sulfur trioxide on the reaction kinetics. For this series, a platinum preconvertor was used to generate feeds with varying sulfur dioxide and trioxide concentrations.

An attempt was then made to fit these data with an equation obtained directly from the law of mass action

$$r = k\,(SO_2)^2\,O_2 - \frac{(SO_3)^2}{Ke}\,. \tag{12}$$

This equation, which they found to fit Knietsch's data, would not fit their data. They then tried Bodenstein's equation,

$$r = k\,SO_2/SO_3\ ^{1/2} \tag{13}$$

which was somewhat better than the law of mass action but still incapable of interpreting the data. Several other forms of rate equations were tried with the best results being obtained with the form

$$r = k\,P_{SO_2} \quad \ln \frac{P^e{}_{SO_3}\,P_{SO_2}}{P_{SO_3}\,P^e{}_{SO_2}}\,; \tag{14}$$

where the superscript e denotes the equilibrium partial pressure. This rate equation also correlates the data of Bodenstein and Fink better than the rate equation proposed by Bodenstein and Fink.

Unfortunately, as pointed out by Uyehara and Watson (55), the total amount of platinum used by Lewis and Ries was not determined. The amount used was constant for all of the experiments making the rate data consistent. However, it is impossible to derive absolute reaction rate constants since the amount of catalyst is unknown.

Taylor and Lenher (54) used a static platinum hot-wire technique to examine the approach to equilibrium from both sides at a temperature of 665°C. They found that the following rate equation best represented their data

$$r = k_1 \frac{P_{SO_2} - P^e_{SO_2}}{P_{SO_3}^{1/2}} - k_2 \left(P^e_{SO_3} - P_{SO_3}\right) \qquad (15)$$

In 1937, Salsas Serra (50) examined the experimental work of Knietsch and Bodenstein and Fink in light of the law of mass action. In opposition to the findings of Lewis and Ries discussed above, he found that the law of mass action adequately represented these data. The law of mass action for the oxidation of sulfur dioxide yields the following rate equation,

$$r = k_1 P^2_{SO_2} P_{O_2} - k_2 P^2_{SO_3}. \qquad (16)$$

Hougen and Watson (26) developed general rate equations for heterogeneous catalysis where one of the elementary reaction steps in the overall series of steps is assumed to be rate controlling. In general, the elementary reaction steps, neglecting mass transfer steps, of the general reaction of A + B to produce C are:

1. The adsorption of either or both reactants on the catalyst surface.

2. The reaction of A + B either both as absorbed species or as one absorbed specie and one gaseous specie.

3. The desorption of the produce from the catalyst surface.

Assuming that one of these steps is rate controlling, i.e., much slower than the other steps while the remaining steps are at equilibrium, a general rate equation can be written for each case. Uyehara and Watson, in a companion paper (55), applied this procedure to the catalytic oxidation of sulfur dioxide. The data of Lewis and Ries were selected for analysis since they were obtained in an apparatus reasonably resembling a differential reactor. The data of Knietsch, Bodenstein and Fink, and Taylor and Lenher were unsatisfactory since they were all obtained in static systems in which concentration and temperature gradients were present. Uyehara and Watson examined each possible rate limiting case and determined that the limiting step is

$$r = \frac{k_1 \left(P_{SO_2}\, P_{O_2}^{1/2} - \frac{P_{SO_3}}{K}\right)}{\left(1 + K_{O_2}^{1/2}\, P_{O_2}^{1/2} + K_{SO_3}\, P_{SO_3}\right)^2} \qquad (17)$$

where K_{O_2} and K_{SO_3} are the absorption equilibrium constants for oxygen and sulfur trioxide respectively. It should be noted that Uyehara and Watson have dropped the sulfur dioxide absorption term from the denominator of the general rate equation. Based on Lewis and Ries' first experimental series looking at the effect of sulfur dioxide concentration, Uyehara and Watson concluded that this absorption term is negligible. Expressions for the coefficients appearing in this equation were updated by Hougen and Watson (25) by the inclusion of Hurt's data (28). Since the mass of Hurt's catalyst was known, an absolute rate constant could be determined. These coefficients are:

$$k_1 = \exp - \frac{8{,}000}{T} + 14.154, \qquad (18)$$

$$K_{O_3} = \exp \frac{20{,}360}{RT} - \frac{23.0}{R}, \text{ and} \qquad (19)$$

$$K_{SO_3} = \exp \frac{16{,}800}{RT} - \frac{17.51}{R}\,. \qquad (20)$$

Boreskov (8) found that the data of Bodenstein and Fink, Taylor and Lenher and Pligunov (unpublished) agreed very well with the rate equation

$$r = k_1 \frac{P_{SO_2}\, P_{O_2}^{0.25}}{P_{SO_3}^{0.5}} - k_2 \frac{P_{SO_3}^{0.5}}{P_{O_2}^{0.25}} \qquad (21)$$

He further states that this equation can be accounted for by assuming that the rate limiting step is the absorption of SO_2 on the catalyst. This equation was also successfully used by Cheslova and Boreskov (11, 12) in the study of catalytic activity of various platinum catalysts.

Roiter, et al., (47) examined the oxidation near equilibrium of sulfur dioxide over a platinum screen by means of a tracer technique using a radioactive sulfur isotope. The kinetics were also examined under non-equilibrium conditions using a standard static measurement technique. The experimental temperature ranged from 600 to 674°C while the initial sulfur dioxide level ranged from 2.7 to 6.3%. The data were then fit to the Boreskov equation with large discrepancies being noted.

A rate equation was then developed assuming that the rate determining step is the surface reaction of adsorbed oxygen and sulfur dioxide

$$r = k \, P_{SO_2} \, P_{O_2}^{1/2} - \frac{P_{SO_3}}{K^e} \qquad (22)$$

This rate equation agreed quite well with the data under equilibrium and non-equilibrium conditions.

At this point in historical review, it is instructive to examine some of the common features of the studies and rate equations reported. One important experimental aspect, which is particularly germane to actual large-scale reactors such as on vehicles, is the neglect of mass transfer effects in the analysis of the data. This neglect of mass transfer may be responsible for the difference in rate equations. For convenience, Table A-8 summarizes the rate equations and pertinent experimental conditions. The effect of mass transfer has been examined in more recent literature and will be discussed later.

All of the rate equations, with the exceptions of Bodenstein and Fink's second equation and Salsas Serra's equation, predict that the forward reaction rate is proportional to the first power of the sulfur dioxide partial pressure. The functional dependency on the oxygen partial pressure is somewhat less clear. Several of the early equations are independent of oxygen partial pressure, however, in these cases the experimental oxygen levels were in large excess. The experimentally small concentration changes due to reaction were almost insignificant in comparison with the large unreacted excess. This and other experimental inaccuracies yielded equations which were independent of oxygen effects. Such was the case of Lewis and Ries' data and analysis. Later analysis of these data by Uyehara and Watson did, however, show an oxygen dependency proportional to the square root of the oxygen partial pressure. This same oxygen functionality was also determined by Roiter where various oxygen concentrations were examined.

In essentially all of the experimental work, a marked reduction was noted with the presence of even very small amounts of sulfur trioxide. Two methods of accounting for this retardation were used in the development rate equation. The first method was to place the sulfur trioxide partial pressure in the denominator of the forward reaction rate term. The second method was to include a reverse-reaction term in the rate equation such as exemplified in the Uyehara and Watson and Roiter equations. The second method also provides mathematical tractability in that the rate can go to zero as equilibrium is approached. The first method, see for instance the equations of Bodenstein and Fink or Lewis and Ries, does not account for equilibrium conditions and, therefore, would be unacceptable.

TABLE A-8

SUMMARY OF RATE EQUATIONS FOR PLATINUM CATALYSIS OF THE OXIDATION OF SULFUR DIOXIDE

Investigator	Rate Equation	Catalyst Description	SO_2 Range	O_2 Range	Conversion Range	Temp. Range
Knietsch [34]	$r = k_1 P_{SO_2} P_{O_2}$	Pt on asbestos	7% + 2-3%	10%	0-99%	300-900°C
Bodenstein and Fink [6,7]	$r = k_1 P_{SO_2} P_{SO_3}^{-0.5}$	Pt mesh, 0.06mm diameter		$P_{SO_2}/P_{O_2} < 3$		150-250°C
Bodenstein and Fink [6,7]	$r = k_1 P_{O_2} P_{SO_3}^{-0.5}$	Pt mesh, 0.06mm diameter		$P_{SO_2}/P_{O_2} > 3$		150-250°C
Lewis and Ries [37,38]	$r = k_1 P_{SO_2} \ln \frac{P^e_{SO_3} P_{SO_2}}{P^e_{SO_2} P_{SO_3}}$	7% Pt on asbestos	<0.5%	air		400-450°C
Taylor and Lenher [54]	$r = k_1 (P_{SO_2} - P^e_{SO_2}) P_{SO_3}^{-0.5} - k_2 (P^e_{SO_3} - P_{SO_3})$	Pt wire				525-700°C
Salsas Serra [52]	$r = k_1 P^2_{SO_2} P_{O_2} - k_2 P_{SO_3}^2$	Analysis of data of Knietsch [34] and Bodenstein [6,7]				
Uyehara and Watson [55]	$r = \frac{k_1}{(1 + P_{O_2}^{0.5} K_{O_2}^{0.5} + P_{SO_3} K_{SO_3})^2} P_{O_2}^{0.5} P_{SO_2} - \frac{P_{SO_3}}{Ke}$	(Analysis of Lewis and Ries data [1-4,5] with inclusion of Hurt data [8-8]				
Boreskov [8]	$r = k_1 P_{SO_2} P_{O_2} P_{O_2}^{0.25} P_{SO_3}^{-0.5} - k_2 P_{O_2}^{-0.25}$	Pt wire				530-850°C
Roiter *et al.* [47]	$r = k P_{O_2}^{0.5} P_{SO_2} - \frac{P_{SO_3}}{Ke}$	Pt screen	1-3%	~19	0-100%	420-700°C
Olsen *et al.* [42]	$r = (P_{SO_2} P_{O_2}^{0.5} - \frac{P_{SO_3}}{Ke}) (B + D P_{SO_3})^{-2}$	0.2% Pt on 1/8 alumina pellets (50,000 v/v/hr.	6.45%	air	4-70	350-480°C

Of the equations discussed, the best with respect to data representation, mathematical formulation and generality is that of Uyehara and Watson. This equation has the general form of the law of mass action and represents the reliable differential reactor data of Lewis and Ries quite well. In addition, the absolute rate constants are available where they are not for several of the other equations.

The effect of diffusion on the overall sulfur dioxide conversion of a large-scale reactor can be determined from the work of Hurt (28). Hurt used the oxidation of sulfur dioxide over platinum as an example of his procedure for correlating the performance of small scale with large scale reactors. An estimate of the influence of mass transfer on the overall sulfur dioxide conversion in a GM reactor can be made using Hurt's kinetic data and mass transfer correlations.

At 40 mph cruise conditions, a typical superficial mass velocity would be 248 lb/hr-ft^2. This represents a particle Reynolds number of 30 for 1/8" pellets. Using Hurt's kinetic correlation and mass transfer correlation, the overall conversion is influenced approximately 25% by mass transfer and approximately 75% by kinetics. Although these values may be in error due to kinetic differences in Hurt's catalyst and automotive catalysts, it does illustrate that mass transfer effects can play a significant role in the formation of automotive sulfates. It also points out that care should be exercised in designing and analyzing kinetic experiments particularly when the goal of the experiment is to predict large-scale reactor behavior from small-scale reactor experiments.

Smith, et al, (1, 22, 29, 42, 52) completed a very comprehensive program involving the design of fixed bed catalytic reactors taking into account heat and mass transfer. The program involved measurement of the chemical kinetics in a differential reactor, examination of diffusional effects, examination of heat transfer effects, and mathematical modeling of an integral reactor incorporating kinetics and heat and mass transfer. The results are of particular interest since the reaction used was oxidation of sulfur over a catalyst of 0.2 weight percent platinum on 1/8" alumina pellets. The platinum was applied such that it penetrated only the outer 1/32" of the pellet. This platinum loading and geometry approximates that of the GM catalyst. In addition, the range of temperature and space velocities spans the range of interest in automotive applications. However, the sulfur dioxide levels were constant and typical of acid plant operations, 6%, and the oxygen levels were those of air. Thus, the only variable investigated was conversion. Overall conversions up to 70% were examined in one paper by using a preconverter ahead of the differential reactor (42). The maximum conversion over the differential reactor was in all but two cases less than 30%.

Olsen, et al., (42) chose to model their results with the rate equation of Uyehara and Watson (55). Since the inlet concentrations to the preconverter were always the same, there existed a definite relationship between p_{SO_2}, p_{SO_3}, and p_{O_2}. Therefore, the Uyehara and Watson equation could be simplified, using the relationship, to

$$ {\frac{p_{SO_2}\, p_{O_2}^{1/2} - \frac{p_{SO_3}}{K}}{r}}^{1/2} = B + D\, p_{SO_3}, \qquad (23)$$

where B and D are constants dependent only upon temperature. Olsen, et al., found that this equation was an excellent representation of their data when the component partial pressures were taken at their interfacial values and not their bulk values, that is to say that diffusion is taken into account.

In a latter paper of this series, Argo and Smith (1) obtained differential reaction rates using larger catalyst pellets than Olson, 1/4" in place of 1/8". These data were then correlated with the Olson data by an activity factor in conjunction with the rate equation of Olson. The activity factor and rate equation correlated both sets of data very well again illustrating that this general equation is capable of describing the catalytic oxidation of sulfur dioxide by platinum. Olson also examined five other rate controlling mechanisms. The data were correlated by rate equations derived from the following rate limiting elementary steps:

1. reaction of adsorbed sulfur dioxide and unadsorbed oxygen (this mechanism yields the Uyehara and Watson rate equation),

2. reaction of adsorbed sulfur dioxide with gas-phase molecular oxygen, or

3. reaction of adsorbed oxygen and gas phase sulfur dioxide.

Unfortunately, the data could not distinguish among these three steps. The data were, however, not correlated by any mechanism which assumes that adsorption or desorption is the rate limiting step.

The differential reaction data were also analyzed by Hurt's (28) method which also accounts for the effect of diffusion. This method failed to correlate the data with the primary objection being that the resistance due to reaction at the catalytic surface was not independent of mass velocity. Olson found that the diffusional effects were better accounted for by using the mass-transfer correlations of Hougen and Wilkie (27). Using these correlations, differences in the sulfur dioxide and trioxide partial pressures between the bulk gas and the catalytic surface were as great as 40% depending upon gas mass velocity, degree of conversion, and temperature. For a GM reactor running at 40 mph, partial pressure differences on the order of ~10% would be predicted for both sulfur dioxide and trioxide. Therefore, this treatment in qualitative agreement with Hart's method indicates that mass transfer can be playing a role in the production of sulfuric acid over the GM type of automotive catalyst.

The mechanism of the oxidation of sulfur dioxide over platinum was examined by Kaneko and Okanaka (31, 32) using a radioactive tracer technique. The experiments were conducted near 400°C in a recirculating reactor using a platinum gauze catalyst of 0.1 mm diameter wire. The kinetic mechanism was examined on both sides of equilibrium, i.e. oxidation of sulfur dioxide and decomposition of sulfur trioxide. The reaction mixture contained only oxygen, sulfur dioxide, and sulfur trioxide with the oxygen and sulfur dioxide always in stoichiometric amounts. In one series of experiments, radioactive sulfur was used to follow the reaction. In the second series, an isotope labelling of oxygen was employed. The combined results of both series show that the rate-determining step is the surface reaction of adsorbed oxygen and adsorbed sulfur dioxide.

In summary, the literature covering the mechanism of sulfur dioxide catalysis by platinum indicates the rate limiting step is the surface reaction between adsorbed oxygen and adsorbed sulfur dioxide. The rate equation which produced the best representation of experimental data was that of Uyehara and Watson (55) which is in agreement with the above rate controlling mechanism. Most of the other rate equations are special cases of the more general Uyehara-Watson equation which further substantiates its validity.

The rate equation indicates two factors which should be considered with respect to automotive sulfate emissions. First, since the rate equation is first order with respect to sulfur dioxide partial pressure, sulfuric acid production will be linearly proportional to fuel sulfur level. Second, since the reaction is half order in oxygen, reducing excess oxygen partial pressure to zero, as is done with the three-way catalyst system, should reduce sulfate emissions to very low levels.

A.5.2 Platinum Catalysis: Automotive Application

Although the literature is void of reaction rate and reaction mechanism studies which relate directly to exhaust oxidation of sulfur dioxide, there are several references covering phenomenological observation of the catalysis of exhaust sulfur dioxide. Chrysler (13), Ethyl (16), Ford (17), and General Motors (18) have made public their data on sulfate emissions as requested in the March 8, 1974 Federal Register. In addition, Pierson, *et al*., (45) and Beltzer, *et al*., (2) have presented SAE papers dealing with automotive sulfate emissions. All of these references, with the exception of General Motors, have examined platinum catalysis only from the standpoint of tailpipe emissions of sulfuric acid. General Motors has conducted a limited amount of laboratory work aimed directly at elucidating the kinetics.

In reviewing these references, there is, for the most part, a common problem in not being able to obtain a balance when catalysts are employed between the sulfur burned in the fuel and the sulfur emitted from the tailpipe. When catalysts are not used, balances can be obtained. Since the majority of the tailpipe sulfur in a non-catalyst vehicle is sulfur dioxide and a sulfur balance can be made, the analytical and test procedures for sulfur dioxide can be assumed to be valid and accurate. The ability then not to be able to close a sulfur balance on a catalyst vehicle is due either to an experimental or analytical problem or to the storage phenomena discussed previously. This problem makes it difficult to assess quantitative catalytic effects from observed tailpipe emissions.

Ford (17, 45) has been able to make sulfur balances for Engelhard IIB-catalyst and non-catalyst vehicles operating under steady cruise conditions. They found that at 60 mph both the Engelhard IIB and GM catalysts converted 44% of the sulfur dioxide to trioxide, which is close to the equilibrium conversion at the test conditions. The GM catalyst at 30 mph converted 84% of the sulfur dioxide which is again very close to the equilibrium value. These conversions were all calculated on the basis of total sulfur out of the tailpipe, thus eliminating the storage problem noted with the GM catalysts.

Ethyl Corp. (16) found that under 40 mph cruise testing, monolithic platinum catalysts converted 43% of the fuel sulfur to exhaust sulfate where conversion is based on total sulfur emitted. Their tests showed that approximately 58% of the fuel sulfur was emitted with the rest being stored. This conversion cannot be compared with equilibrium since the catalyst temperature was not given. The magnitude of these results are in line with Ford's findings.

Beltzer, *et al*., (2) have also measured sulfate emissions for steady cruise conditions. Sulfur dioxide measurements were not made precluding making a sulfur balance. The sulfate emissions at 60 mph for the pelletized oxidation catalyst agree fairly well with those obtained by Ford using approximately the same fuel sulfur level. If the storage effects are similar then by implication, this conversion is also close to equilibrium.

The GM (18) extended 60 mph cruise tests on their catalysts show a large spread both in sulfate conversion and in sulfur balances. In general, average conversions based on sulfur emitted were in the range of 20 to 40%. This is somewhat lower than the conversions discussed above, but still represents a significant approach to equilibrium.

The Chrysler reference (13) did not present conversion data for steady cruise conditions. A consensus of these references shows that the reaction rate is of sufficient magnitude that the oxidation of the exhaust sulfur dioxide approaches equilibrium in actual vehicle operation. Due to the storage effect together with possible analytical problems, a more quantitative assessment of the reaction rate is impossible.

In addition to their vehicle work, GM (18) also reported some preliminary parametric studies using a laboratory-scale reactor. They also caution the reader that the analytical methods caused significant uncertainties in the sulfur trioxide measurements. The storage problem was also a large factor. In one instance, less than 30% of the inlet sulfur could be accounted for.

GM examined the conversion both as a function of temperature and space velocity using actual vehicle exhaust. They found that the conversions, based on measured sulfur trioxide and average sulfur input, were between 5 and 15% with only a weak temperature dependency. From analysis of these data, with respect to temperature and space-velocity dependency, it was concluded that the reaction is kinetically controlled. The effect of platinum loading was also investigated by increasing the loading from 0.1% to 1.0% platinum. The observed effect was only a very slight increase in measured sulfur trioxide. This finding is in contradiction to a kinetically controlled reaction. If the reaction were kinetically controlled for both loadings, then an order of magnitude change in platinum loading would change the rate by an order of magnitude. Invariance to loading conforms with either a diffusion or equilibrium controlled reaction.

It is informative to examine these data assuming that the outlet sulfur trioxide is the difference between the outlet sulfur dioxide and the total inlet sulfur. This assumption could be valid if the sulfur trioxide analyses were in error and no storage was taking place. Under this assumption, conversions are all very near equilibrium indicating that the reaction is equilibrium controlled. Some credibility must be assigned this probability since GM's platinum loading data also indicate an equilibrium controlled reaction. However, since the storage problem is real and the data severely limited, this assumption may not be entirely valid. Nonetheless, the possibility exists that more sulfur dioxide is being produced than the GM data indicate.

The form of the rate equation describing the catalysis reaction can, to a limited extent, be deduced from the above studies. The results of Beltzer, Ford, and GM show that sulfate emissions increase with gasoline sulfur level. Beltzer and Ford find that conversion appears to be invariant with respect to fuel sulfur level which means the reaction rate is proportional to the first power of the sulfur dioxide partial pressure in agreement with the rate equations previously discussed. The quantitative effect of oxygen partial pressure can be assessed from GM's vehicle and laboratory studies. These studies show that reducing the partial pressure of oxygen over the catalyst reduces sulfate emissions and the reaction rate. The quantitative dependency on the reaction rate cannot be determined due to the limited data of dubious accuracy.

In summary, the use of a platinum automotive-exhaust catalyst does result in oxidation of fuel sulfur to yield sulfur trioxide. The extent of this oxidation is clouded by the problems of sulfur storage and inaccurate analytical techniques. Results showing anywhere from 10% to complete approach to equilibrium have been observed. The variability of these data precluded any quantitative analysis of the reaction rate, however, the data did indicate the form for the reaction-rate equation. The rate equation should be linear with respect to sulfur dioxide partial pressure and should be proportional to some positive power of the oxygen partial pressure. This form is in agreement with the rate equations obtained in the industrial catalysis section.

A.6 Sulfate Trap

There are two conceivable means of removing the sulfuric acid from a vehicle's exhaust system. The first is by the use of particulate traps in which the condensed acid is removed as droplets. The second is by reaction of the acid either as sulfur trioxide, gaseous sulfuric acid, or condensed, liquid sulfuric acid with a suitable sorbent. The capacity of either type of trap can be conservatively estimated for 50,000 miles by assuming an overall fuel economy of 10 miles per gallon. If the fuel sulfur level is taken as the industry average of 0.03 weight percent, and it is assumed that the worst possible case of total conversion exists, then 4.2 kgm or 131 gm. moles. of sulfur will be consumed and must be trapped.

The particulate trapping technique has several serious problems associated with it which preclude its use in automotive applications. The sorbent trap method is more attractive. Consideration of several important properties which a sorbent material must process shows that the most promising sorbent material is calcium oxide. Other attractive sorbents are the oxides of magnesium, manganese, and aluminum.

A.6.1 Particulate Trap

There are several very serious problems associated with collecting these sulfuric acid emissions with a particulate trap. The largest problem is that the sulfuric acid exits the tailpipe in the gas phase for the majority of driving conditions. This has been discussed previously. Therefore, for a particulate trap to be feasible, an exhaust heat exchanger would be required. Assuming condensation is possible, then the condensed acid must be separated from the exhaust gas by some means. This separation will be exceedingly difficult due to the extremely small particle size of the condensed acid. Typically, the particle sizes for the effluent of acid plants is less than 2 microns for 85 to 90% of the acid by weight (53). Ford (17) found that >90% of the exhaust sulfate mass was less than 0.25 microns. The problems associated with this separation would be almost unsurmountable given the space limitations and low back-pressure requirement. Assuming these problems can be overcome, the problem then becomes one of containing the liquid acid. Assuming the acid would be diluted by 50 weight percent water, the volume of acid solution collected over 50,000 miles would be 18.5 liters. Not only must this be contained, it must be protected from further dilution with water during cold starts and shut downs. Based on all of these problems, it is not feasible to use particulate traps to remove automotive sulfate particulate.

A.6.2 Sorbent Trap

The second method of reducing exhaust sulfate particulate is to trap the sulfur trioxide or sulfuric acid by chemical reaction with a solid sorbent material. In this manner, the potential sulfate particulate is trapped and stored in the exhaust system as a solid material. The obvious sorbents to consider for this application are solids which are chemically basic. While there are only a few references in the literature concerning the reaction of basic materials with either sulfur trioxide or gaseous sulfuric acid, there are numerous references to reactions with sulfur dioxide. The majority of these references are concerned with the selection of potential sorbent material for the removal of sulfur dioxide from various stack gases. Since the general reaction of either oxide is a gaseous acidic component reacting with a basic solid component and since the trioxide or gaseous acid is more acidic than the dioxide, then it would be expected that suitable sulfur dioxide sorbents would also serve as suitable trioxide sorbents. In fact, several researchers (3, 44) have found that the reactivity of the trioxide is orders of magnitude greater than that of the dioxide. Thus, the literature of sulfur dioxide removal will be used as a basis for selecting potential sulfate trap sorbents.

In selecting potential sorbents for automotive exhaust application, there are several important factors which must be considered. These factors are 1 - activity for sulfur trioxide or sulfuric acid removal, 2 - thermal stability, 3 - volume and weight restrictions, 4 - potential side reaction, 5 - water solubility, 6 - cost and availability of sorbent, and 7 - toxicity of fresh or sulfated sorbent. The importance of the first factor goes without saying, a sorbent must be able to sorb over the temperature range encountered in automotive exhaust. The thermal stability of the sulfated sorbent is also vital to potential sorbents. The sulfated sorbent must not begin to decompose at temperatures below the maximum expected operating temperature of the catalyst. With this restriction, sulfated sorbents which decompose at temperatures below 800°C will not be considered.

Since the sulfate trap must be located in the exhaust system on the underside of the vehicle where space is limited, volume and weight restrictions are important. Another important factor to consider in the selection of sorbent materials is the possibility of side reactions with exhaust gas constituents such as water or carbon dioxide to form stable compounds. Such reactions would use potential sulfate sorbent and decrease the sulfation capacity of the trap.

The water solubility of the fresh and sulfate sorbent material must be considered. There are several conditions in which part or all of the sulfate trap could be exposed to liquid water. If the sorbent is appreciably soluble, then the potential sulfate capacity can be decreased. This leaching of material can also lead to problems in maintaining the structural integrity of some possible trap configurations.

Since a successful sulfate trap has the possibility of being installed on millions of vehicles, the cost and availability of the sorbent must be considered. Thus, expensive metals such as gold or silver or materials available in limited quantities such as various rare earth elements cannot be considered.

Since the trap represents a potential source of particulate emissions due to fresh or sulfated sorbent attrition, the toxicity of the fresh and sulfated sorbent as well as other possible sorbent compounds must be considered. For instance, beryllium would be ideal from the volume-weight aspect due to its low molecular weight and divalency. However, it and its compounds are extremely toxic (51) and, hence, cannot be considered as potential sorbents.

With these factors in mind, the literature has been reviewed to select possible candidate sorbents to be used in a vehicle sulfate trap. There are several comprehensive references (8, 4, 21, 40, 44, 59, 60) in the literature in which a wide variety of potential sulfur dioxide sorbents have been examined. These studies were all aimed at removing sulfur dioxide in the concentration range of 1 to 5 percent from a stack gas. Although these studies are for a higher concentration and a different oxide of sulfur, the activity results can be readily extrapolated to the sorption of sulfur trioxide from automotive exhaust.

The major chemical classification of the sorbent compounds investigated are the metal oxides. The sorbent material is envisioned as being installed in the system either as the oxide or as the metal which will readily oxidize in the oxidizing exhaust atmosphere. The general sorption reaction can be written as

$$MeO + SO_3\ (g) \longrightarrow Me\ SO_4 \qquad (24)$$

where Me is a general symbol representing any sorbent metal. Lowell, et al. (40) evaluated the oxides of 47 elements for potential use as sulfur dioxide sorbents. Their thermodynamic calculations show that the formation of sulfates for nearly all of the elements considered is favorable. Pechkovsky (44) examined the rate of sulfation of several metal oxides in powder form over a temperature range of 400-1000°C. He found that calcium oxide was more active than magnesium oxide which was more active than zinc oxide.

The Bureau of Mines (4) conducted a program looking at the activity of several bulk oxides with respect to their ability to sorb sulfur dioxide. Experimentally, a bed of sorbent, 8-24 mesh particles, was exposed to a synthetic flue gas with 0.3 volume percent sulfur dioxide. The space velocity was maintained at 1,050 v/v/hr and temperatures of 130 and 330°C were examined. Typical results showed that active sorption materials would remove essentially all of the sulfur dioxide for a period of time. As sulfation of the sorbent proceeded, a point was reached where breakthrough would occur. From this point, the fraction of sulfur dioxide removed was found to decrease linearly with time.

The sorbent materials were rank ordered with respect to the amount of sulfur dioxide removed per unit mass of sorbent at the point of 90% removal of sulfur dioxide. The most active sorbents in order of activity were the oxides of manganese, cobalt, and copper.

The temperature study showed that for most sorbents approximately twice as much sulfur dioxide had been sorbed up to the 90% breakthrough point at 330°C than at 130°C. At the higher temperature, it was also noted that the sulfur dioxide had made a significant penetration into the particles of the more active sorbent materials.

Vogel, et al., evaluated the activity of several metal oxides supported on alumina. All test samples were made with the same metal equivalents so the various materials could be directly rank ordered as to activity. Samples of each supported sorbent were exposed to a synthetic stack gas and the outlet was continuously analyzed for sulfur dioxide. From these data, the sulfate loading of each sorbent was determined for the conditions where the outlet sulfur dioxide concentration was five percent of the inlet concentration. In addition, the maximum loading was determined by extrapolation of the data.

The materials were then rank ordered as to the percent of sorbent reacted at the five percent breakthrough point. This ranking also agreed with the ranking based on percent of sorbent reacted at maximum sulfation capacity with one exception. The one exception was the Bureau of Mines alkalized alumina sorbent which was included in this study as a benchmark. This material has been extensively studied (4, 5, 43, 40) as a sulfur dioxide sorbent but would not be acceptable as a vehicle trioxide sorbent due to its low sulfation capacity per unit volume.

The activity of the sorbents in order of decreasing activity is: the oxides of sodium, strontium, copper, calcium, and chromium. All of these materials had in excess of 50% of the sorbent reacted at the 5% breakthrough point. These were followed by the oxides of : barium, lead, cadmium, manganese, magnesium, iron, cobalt, nickel, and zinc. Tin and vanadium oxides showed no apparent activity. The alumina substrate was also tested and found to be completely inactive. In general, these results show that the alkali and alkaline earth metals exhibit highest reactivities. In addition, copper and chromium showed good reactivity.

Welty (60) conducted a theoretical study of the reactivity of potential sorbent cations based on a characterization factor consisting of the cation radius, electronegativity, and valence. Using this factor, the alkali metals are the most promising sorbents followed by the alkaline earth metals, then by various transition metals. This reactivity scale is in general accord with the experimental and theoretical works described previously.

The second necessary property a sorbent must have is thermal stability of the sulfated material. Although the temperature regime the sorbent sees in vehicle use can to some extent be controlled by location in the exhaust system, the sulfated material must have a higher decomposition temperature than it is expected to experience. Temperatures at or near the exit of the exhaust pipe can be as high as 800°C under sustained high speed driving of vehicles equipped with oxidation catalysts. Therefore, the sulfated sorbent must have a decomposition temperature at or above 800°C.

Table A-9 lists the decomposition temperatures of several sulfated sorbents. The temperature ranges and slight disagreement between references are due to the difficulty in experimentally determining decomposition temperature and in the different experimental methods employed. These results show that the sulfated alkali and alkaline earth metals all show acceptable decomposition temperatures. The transition metals, however, show borderline temperatures, particularly aluminum oxide. If these materials are to be considered, their installation would have to be limited to points as far from the oxidation catalysts as practical.

As estimated above, the sulfate trap must have the capacity to react with 131 g moles of sulfur. Table A-10 lists the mass of typical sorbents which would fulfill this requirement. In addition, the volume of sorbent as calculated using the crystalline density is included. In the cases where more than one crystal structure exists, an average density was used. There are several important general conclusions which can be arrived at from an examination of this table. Within a given group of the periodic table, the required amount of the lower molecular weight sorbents are lighter and of lower volume. For instance, the required mass and volume of sodium oxide are 8.12 kg and 3.58 litres whereas the higher molecular weight cesium oxide requires 36.9 kg and 8.69 litres.

Another important consideration is the valence of the sorbent cation. For instance, two univalent cations are required for each sulfate anion whereas only one divalent cation is. If these cations have approximately the same molecular weight, then the divalent one would be preferable. An excellent example is the third period of the periodic table. The first three members of this period, sodium, magnesium, and aluminum, have nearly the same atomic weight but they are, respectively, univalent, divalent, and trivalent. The required amount of sodium oxide is 8.12 kgm, of magnesium oxide is 5.28 kgm, and of aluminum oxide is 4.45 kgm. The volumes likewise decrease. Therefore, to minimize trap mass and volume, lower cation molecular weight sorbents with higher valence states are preferred.

There is another problem which must be considered in the selection of a sorbent material and in the engineering of the sorbent structure to be installed in a vehicle. This problem is the increase in volume of the sorbent as sulfur is picked up. The magnitude of this problem is shown in Table A-10 where the volumes of the totally sulfated sorbents are given along with the ratio of the sulfated volume to the fresh sorbent volume. This volume increase is a result of two compounding factors. First, the mass of the trap is continuously increasing due to the pickup of sulfur trioxide and dioxide. Second, the crystalline density of the sulfate is always less than the corresponding oxide.

TABLE A-9

DECOMPOSITION TEMPERATURES OF SULFATED SORBENTS

Compound	Decomposition Temperature	Determination Method	Reference
Sodium	>800°C		40
Potassium	>800°C		40
Cesium	>800°C		40
Magnesium	750°C	Thermodynamic Calculation	60
	890-972°C	In air flow	3
Calcium	1180	Thermodynamic Calculation	60
	>1200°C	In air flow	3
Barium	>800°C		40
Aluminum	652	Vacuum	58
	590-639°C	In air flow	3
	650-950°C	Inert gas flow	40
Manganese	699-790°C	In air flow	3
	880-1100°C	In air	40
Iron	630	Vacuum	58
	781-810°C	Inert gas flow	40
	702-736°C	In air flow	3
	700-840°C	In air	40

TABLE A-10

MASS AND VOLUME REQUIREMENTS OF VARIOUS SORBENTS*

Sorbent Material	Mass Req'd., Kg	Vol. Req'd., l	Sulfated Mass, Kg	Sulfated Vol., l	Sulfated Volume, Expansion Ratio
Na_2O	8.12	3.58	18.6	6.94	1.94
K_2O	12.34	5.32	22.8	8.58	1.61
Cs_2O	36.9	8.69	47.4	11.2	1.29
MgO	5.28	1.48	15.8	5.93	4.00
CaO	7.35	2.21	17.8	6.46	2.92
BaO	20.1	3.51	30.6	6.79	1.94
Al_2O_3	4.45	1.12	14.9	5.51	4.92
MnO	9.29	1.70	19.8	6.09	3.58
Fe_2O_3	6.97	1.33	17.5	5.64	4.24
CuO	10.4	1.63	20.9	5.80	3.56
ZnO	10.7	1.90	21.1	5.97	3.14
$MgCO_3$	11.0	3.73	15.8	5.93	1.59
$CaCO_3$	13.1	4.65	17.8	6.46	1.39
$BaCO_3$	25.9	5.84	30.6	6.79	1.16
Na_2CO_3	13.9	5.48	18.6	6.94	1.27
K_2CO_3	18.1	7.46	22.8	8.58	1.15

*Assuming 131 g moles of sulfur to be trapped.

Unfortunately, the magnitude of this volume increase problem increases for the more desirable (from initial volume and weight considerations) sorbents. For instance, aluminum oxide has the lowest volume required, yet has the highest volume increase ratio. On the other extreme, cesium oxide has the largest volume requirement, yet the lowest expansion ratio.

One means of minimizing this problem is to provide for this expansion chemically by using a sorbent which gives up some mass as it picks up the sulfur oxides. This exchange reaction must release a compound which itself is not a deleterious emission. One class of ideal exchange sorbents are the metal carbonates which release carbon dioxide in exchange for sulfur oxide. Several potential carbonates are listed in Table A-10 where their volume and mass requirements are shown. It is immediately obvious that the volume and mass of the carbonate sorbents is much greater than for the oxide, however, the volume expansion is drastically reduced. Use of the carbonates would simplify the engineering of the physical sorbent structure by eliminating the need for large volume expansions. This simplification more than outweighs the initial increased volume of the sorbent carbonates over the oxides.

There are two side reactions of the sorbent with exhaust gas constituents which need to be considered in selecting potential sorbent materials. The first side reaction is the reaction of the sorbent oxide with carbon dioxide to form the sorbent carbonate. This reaction is important for several reasons. If the carbonate is unreactive towards sulfur trioxide, then formation of carbonate decreases the potential sulfation capacity of the trap. If the sorbent carbonate is reactive, it is possible that the reactivity will be lower than for the sorbent oxide which would lower the reactivity of the trap. Another problem is that the formation of carbonate causes a volume expansion. This expansion within a sorbent particle causes the pore volume to decrease which, in turn, can hinder diffusion of the sulfur trioxide into the particle. Therefore, the potential amount of internal sulfation will be decreased.

The best example of carbonation is the reaction of calcium oxide. Thermodynamic calculations show (see for instance Ref. [46]) that the carbonation of calcium oxide is favorable in an exhaust gas environment at temperatures below 760°C. Thermodynamic calculations also show that the calcium carbonate formed will react with the oxides of sulfur. Thus, the possibility of carbonate formation exists and will be competitive with the sulfation. If the carbonate is formed, it can also react with the sulfur oxides. However, the possibility exists that this reaction will be significantly slower than the reaction with the oxide which would lower the overall activity of the trap. There are no rate data available which are applicable to exhaust gas concentrations and temperatures. Therefore, the possible activity reduction cannot be determined or estimated.

TABLE A-11

SOLUBILITIES OF VARIOUS FRESH AND SULFATED SORBENTS
SOLUBILITIES IN GRAMS PER 100 ML. OF COLD WATER

Sorbent Material	Oxide Solubility	Carbonate Solubility	Sulfate Solubility
Sodium	d.*	7.1	S.
Potassium	v.s.	112	12
Cesium	v.s.	260.5	167
Magnesium	0.00062	0.0106	26
Calcium	0.131	0.0015	0.209
Barium	3.48	0.002	0.0002
Aluminum	i	----	31.3
Manganese	i	----	52
Iron	i	0.0067	sl. s.
Copper	i	i	14.3
Zinc	0.00016	0.001	S

* d. - dissolves
v.s. - very soluble
S. - soluble
sl.s - slightly soluble
i - insoluble

The amount of pore volume reduction due to volume increase upon carbonation can be estimated from Table A-10. For the same equivalent of calcium, the carbonate requires 2.10 times the volume of the oxide. Therefore, if the initial particle of calcium oxide had a porosity of 50%, complete carbonation would fill all of the pore volume assuming all expansion is internal and no reaction occurs with sulfur oxides.

These same problems are also present with essentially all potential sorbent oxides. Since the desired type of sorbent reaction, a basic sorbent with the acidic sulfur oxides, is the same as for carbonation, potential sulfur oxide sorbents will also react with carbon dioxide.

The second detrimental side reaction is that of either the fresh or sulfated sorbent with water. The main problem associated with the reaction of water is the volume expansion of the bed at low temperatures such as during startup. Several of the sorbent oxides can react with water to form hydroxides and most of the sulfated sorbents are highly hydroscopic and form hydrates with as many as 18 molecules of water per molecule of sulfated sorbent (i.e., $Al_2(SO_4)_3 \cdot 18\ H_2O$). These added water molecules cause a volume increase which can plug pores and even increase pressure drop across the catalyst bed. Since the water of hydration is driven off even at very low temperatures, the problem of volume increase would be applicable only at startup.

Both possible side reactions apply to almost all potential sorbents. The degree to which these reactions would decrease the activity and/or capacity of a sulfate sorbent is a very complex question which cannot be answered without direct experimentation under exhaust gas conditions. Since all potential sorbents could exhibit these problems to some unknown degree, a selection of potential sorbents using the criterion of deleterious side reactions is impossible.

Since the sulfate trap must operate in an environment where contact with liquid water is highly probable at many times during the lifetime of the trap, the fresh and sulfated sorbent should be insoluble. Dissolution of the fresh sorbent would decrease the total sulfation capacity of the trap. Dissolution of either or both the fresh and sulfated sorbent would decrease the structural strength of the sorbent particles possibly leading to increased attrition and/or channelling.

The solubilities of several potential sorbent oxides, carbonates and sulfates are given in Table A-11. These values were all obtained from reference (1). The table shows that the oxides, carbonates, and sulfates of the alkali metals are all quite soluble with the solubility increasing with increasing molecular weight. The alkaline earth oxides show more favorable solubilities. Magnesium and calcium oxides have acceptable solubilities. Barium oxide is more soluble and could present some problems. The carbonates of the alkaline earth series all have acceptable solubilities. The solubilities of the sulfates decreases with increasing molecular weight. The solubility for magnesium sulfate would be borderline while the higher molecular weight members would be acceptable.

The oxides and carbonates of the transition metals are insoluble or, at worst, only slightly soluble. The sulfates are, however, quite soluble with the exception of iron which is only slightly soluble.

Based on solubility restrictions, none of the alkali metals would be acceptable. Calcium of the alkaline earth metals would be acceptable, and iron of the transition metals listed would be acceptable.

Another consideration of somewhat lesser importance in selecting potential sorbents is the cost and availability of materials. The real importance of cost and availability would come if two sorbents were to show equal potential. However, for screening purposes, only those materials which are in short supply or are very costly should be eliminated.

For reference, the costs of several potential sorbent materials are listed in Table A-12. The cost listed is for enough material to trap 131 g moles of sulfur. All material costs were obtained from Reference (9) and pertain to bulk quantities f.o.b. New York. The first cost column assumes that the trap material can be prepared by some simple mechanical treatment, e.g. pelletization. The costs for the transition metals are based on the bulk metal rather than the oxides. The second cost column was developed assuming that a soluble salt, in this case the nitrate, would be required as the raw material in a precipitation procedure.

The first cost column shows that the least expensive sorbents would be the oxides of the alkaline earth metals followed by the transition metals. In all cases, the cost of the soluble nitrate salts were higher than for the oxides. Also, the cost of preparing the sorbent from the salt would be greater than from the oxide.

Ideally, the construction of the trap would preclude fresh or sulfated sorbent attrition. However, in practice attrition and emission of the trap material will occur. Therefore, emissions of the fresh and/or sulfated sorbent cannot be harmful. Two examples immediately stand out: beryllium and lead. Beryllium, the lowest molecular weight alkaline earth metal, would be an ideal sorbent cation from many of the considerations discussed above. However, beryllium oxide and sulfate are extremely toxic (57) and, therefore, must be eliminated from consideration. The same is true for lead. The lead oxide candle procedure for quantitative sulfur dioxide measurement shows an excellent sorptive activity but lead oxide and sulfate emissions are harmful. Hence, lead must also be eliminated as a potential sorbent.

Table A-12

ESTIMATED COSTS OF VARIOUS SORBENTS

Sorbent	Molecular Weight	Kg of Sorbent per trap	Estimated Sorbent Cost, $	Sorbent Cost as Nitrate Salt, $
MgO	40	5.2	0.50	14.00
CaO	56	7.3	0.20*	---
BaO	153	20.0	6.80	11.00
Ni	59	7.7	27.00	23.00
Cu	64	8.4	10.00	23.00
Zn	65	8.5	6.50	7.70
Mn	55	7.2	5.20	---

* from limestone

In selecting potential sorbents based upon these considerations, there is no single material which stands out in all categories. The one cation which is consistently near the top in all categories is calcium. This cation could be employed either as the oxide or as the carbonate. Other potential sorbents which show promise are magnesium, manganese, and aluminum. Again, the most probable sorbent would be the oxide of these materials. The remaining potential sorbents have deficiencies in one or more categories.

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APPENDIX B

MEASUREMENT TECHNIQUES

B.1 Gaseous Emissions

Gaseous emissions were measured using standard instrumentation for Federal Emission Test Procedures. CO and CO_2 were analyzed by NDIR, hydrocarbons by FID, and NO_x by chemiluminescence.

B.2 Measurement of Sulfate Emissions

Sulfate emission samples were collected using Exxon Research's exhaust particulate sampling system, and also by the Goksøyr-Ross technique. The sulfate content of samples collected by both methods was determined by colorometric titration using Sulfanazo (III) as an indicator. Each of these techniques is described in detail below.

B.2.1 Exhaust Particulate Sampling System

The exhaust particulate sampling system has been designed to collect particulate matter at constant temperature during the 1972 and 1975 Federal Test Procedure, and 64 km/h (40 mph) cruise conditions. This system is capable of frequent and convenient operation, and is compatible with constant volume sampling (CVS) of auto exhaust. Compatibility is obtained because the particulate sampler requires only a small portion of the diluted exhaust, the major portion of the sample is available to the CVS system for the measurement of gaseous emissions. Conditions used in the measurement of exhaust particulate conform to those mandated by the Federal Test Procedures for gaseous emissions.

This sampling system uses a small tunnel which means that low dilution ratios are used, allowing gaseous emissions such as CO, hydrocarbons, NO_x and SO_2 to be measured accurately. While low dilution ratios are desirable from the standpoint of CVS gaseous emission measurements, the collection of a proportional sample of particulate matter at constant temperature 32°C (90°F) from a sample stream having a high dew point without causing condensation of water requires an advanced temperature control system.

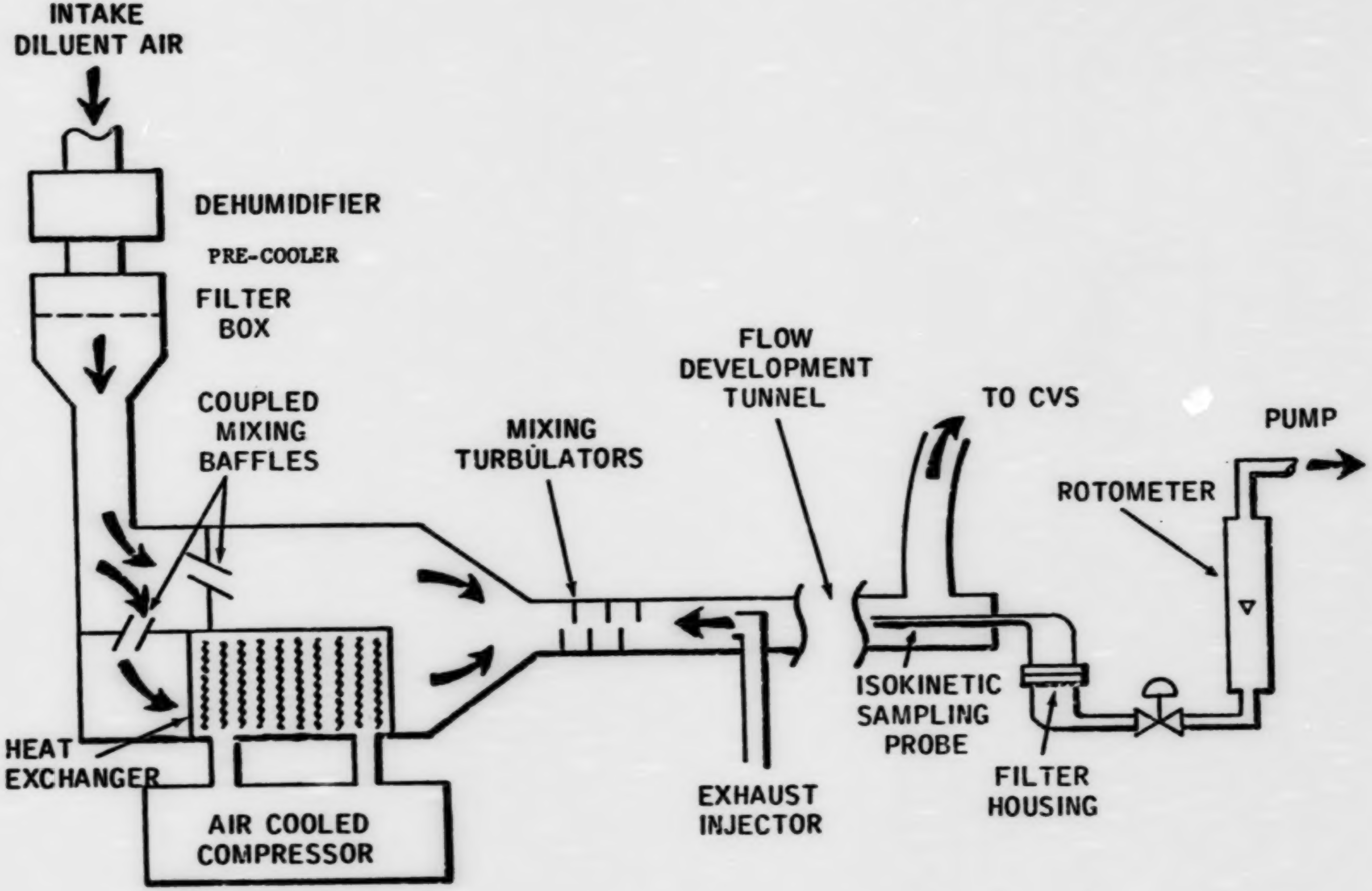
B.2.1.1 Sampling System Components

The particulate sampler which has been discussed previously (1,2) is shown schematically in Figure B-1. This system has five major components:

1. A diluent air preparation system
2. A flow development tunnel
3. An exhaust injector system
4. An isokinetic sampling probe
5. A particulate measuring device, which in the case shown is a 0.2 micron glass fiber filter

FIGURE B-1

EXHAUST PARTICULATE SAMPLER


INTAKE
DILUENT AIR
DEHUMIDIFIER
PRE-COOLER
FILTER
BOX
COUPLED
MIXING
BAFFLES
HEAT
EXCHANGER
AIR COOLED
COMPRESSOR
MIXING
TURBÜLATORS
FLOW
DEVELOPMENT
TUNNEL
EXHAUST
INJECTOR
TO CVS
ISOKINETIC
SAMPLING
PROBE
FILTER
HOUSING
ROTOMETER
PUMP

The overall function of this system is to allow the collection of particulate matter from an isokinetically sampled portion of diluted exhaust which has been cooled to 32°C by dilution with chilled, dehumidified, filtered air. The function of each of the components in accomplishing this objective is described below.

B.2.1.2 Diluent Air Preparation System

This system consists of a dehumidifier, filter, coupled mixing baffles, a cooling system, and mixing turbulators.

The dehumidifier shown schematically in Figure B.2 minimizes the possibility of condensation occurring in the sampling system during a run, and is an integral part of the temperature control system. Diluent air is dried by passage through a filter and a slowly rotating desiccant wheel containing laminated flat and corrugated asbestos, impregnated with a regenerable desiccant, LiCl. Dehumidification of diluent air and desiccant reactivation are concurrent processes, so that dehumidification can be carried out on a continuous basis. The dehumidifier, a Honeycombe Model HC 750-EA is manufactured by Cargocaire Engineering Corporation is described in their Bulletin No. 07169(3).

Dehumidified inlet air passes from the dehumidifier to a filter box containing a paper filter, a bed of activated charcoal, and a second paper filter. This assembly is the standard filter box assembly for the Scott Research Constant Volume Sampler (CVS) unit. The filter assembly removes the particulate matter present in the diluent air and reduces and stabilizes the background hydrocarbon content of the diluent air.

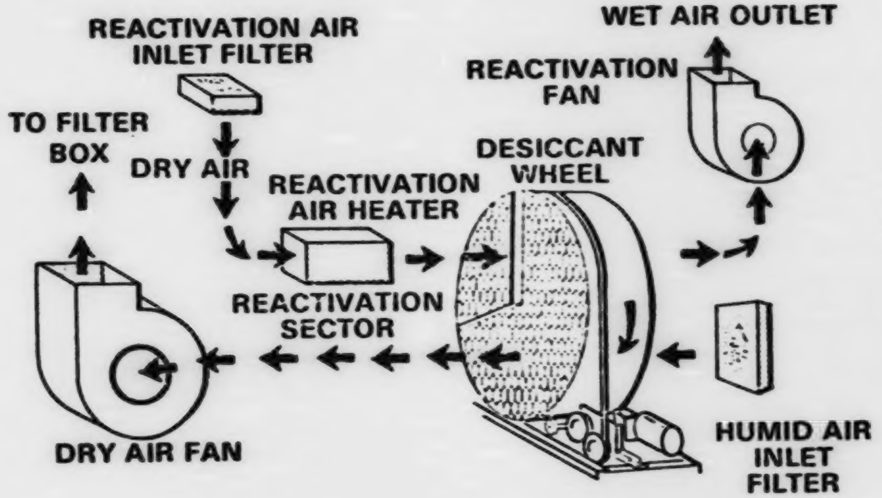
Because regeneration of the desiccant is accomplished by heating, the dehumidified air emerging from the drum is above ambient temperature. A pre-cooler situated between the dehumidifier and the CVS filter cools the dehumidified air stream down to ambient temperature to take the additional cooling load imposed by the dehumidification step away from the final cooling system. The pre-cooler consists of several rows of coils through which chilled city water is passed.

The coupled mixing baffles continuously divide the dehumidified, filtered air into two portions, one which passes through the cooling system, and a second portion which bypasses the cooling system. The position of the mixing baffles is controlled by a rapid response, deviation-type controller operating on an input signal from a thermocouple in the filter housing. The system is designed to maintain 32°C at the filter housing, during the 1972 or 1975 Federal Test Procedures, and 64 km/h cruise.

The controller operates by comparing an input signal from a thermocouple in the filter housing with a set point signal, and takes corrective action to either raise or lower the output signal until the set point and thermocouple input are equal. The controller used was an Electronic Control System Model 6700 Controller(4). The output signal

FIGURE B-2

SCHEMATIC OF DEHUMIDIFICATION SECTION


REACTIVATION AIR INLET FILTER
WET AIR OUTLET
REACTIVATION FAN
TO FILTER BOX
DRY AIR
DESICCANT WHEEL
REACTIVATION AIR HEATER
REACTIVATION SECTOR
DRY AIR FAN
HUMID AIR INLET FILTER

from the controller is fed to an electric to pneumatic transducer (5) which in turn activates a pneumatic controller (6) which operates the coupled baffles.

The cooling system is an air cooled condensing evaporator which has a cooling capacity of 8,300 kcal/hr. The evaporator is a Dunham-Bush, Model SCO-50C unit (7) containing ten rows of custom-made cooling coils (8).

The mixing turbulators insure that chilled air is thoroughly mixed with the portion of air bypassing the cooling system before the stream is used to dilute the vehicle exhaust. The turbulators consist of six semi-circular perforated plates attached to a 1/2" diameter wall tube at their centers, arranged in a helical series sequence along the tunnel axis. This arrangement allows both longitudinal and latitudinal mixing.

Maximum flow through the diluent air preparation system is determined by the cooling capacity of the chiller. Presently, this limitation is about 13 m^3/min.

B.2.1.3 Flow Development Tunnel

The exhaust and diluent air are mixed and a uniform velocity profile is developed in the flow development tunnel. The flow development tunnel is a 2.23 m long section of a 4-inch diameter Schedule 5 (actual I.D. = 11.0 cm) stainless steel pipe. Neither the length nor the diameter of the flow development tunnel have been optimized, but as will be shown in another section, a dilution tunnel of these dimensions is satisfactory for this purpose.

B.2.1.4 The Exhaust Injection System

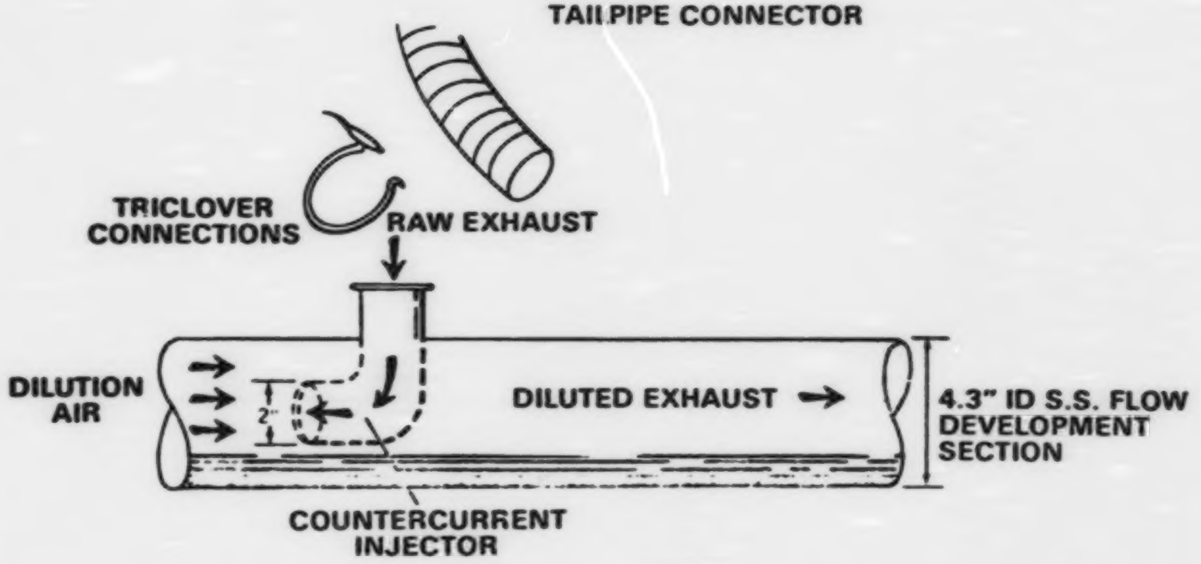
The raw exhaust is mixed with the diluent air normally used in the CVS in such a way as to completely mix the two in as short a time interval as possible. This is accomplished by injecting the exhaust in a countercurrent direction to the diluent air stream. Previous experiments (1) have shown this to be the most efficient way of obtaining a rapidly mixed, uniformly distributed diluted exhaust sample stream. Figure B-3 shows a schematic of the exhaust injector in the countercurrent position.

B.2.1.5 Isokinetic Probe

Isokinetic sampling is required to insure that the particulate sampled is representative of the particulate in the main stream; that is, the particulate concentration and size distribution in the probe sample should correspond to that of the main stream. The probes are designed so that the sample stream is divided into two parts with a volume ratio equal to the ratio of the cross-sectional areas of the openings of the sample probes and the tunnel cross-sectional area, that is

FIGURE B-3

COUNTER CURRENT EXHAUST INJECTION SYSTEM


TAILPIPE CONNECTOR
TRICLOVER CONNECTIONS
RAW EXHAUST
DILUTION AIR
2"
DILUTED EXHAUST
4.3" ID S.S. FLOW DEVELOPMENT SECTION
COUNTERCURRENT INJECTOR

$$\frac{\text{Area (probe)}}{\text{Area (tunnel)}} = \frac{\text{Flow Rate in SCFM (probe)}}{\text{Flow Rate in SCFM (tunnel)}}$$

Another problem to be considered in probe designs is minimizing sample deposition in the probes. When suspended particulate matter leaves the tunnel and enters the sampling probe, it is leaving a low surface to volume region and entering a high surface to volume region. Relative sample losses by impaction should be greater in the probe than in the tunnel. Therefore, the probe should be as short and direct as possible to minimize the residence time of the particulate matter in the probe. The filter housing connected to the probe is flared out as soon as physically possible to minimize the surface to volume ratio of the housing and thereby reduce sampling losses by impaction in this portion of the sampling system.

B.2.1.6 Particulate Collecting Stage

At present, particulates are collected by filtering the sample through pre-weighed filters. In principle, other particulate collectors such as impactors and other devices, could be utilized with the particulate sampling system. In this paper, total particulates are determined gravimetrically using Gelman Type E glass fiber filters which have an effective porosity of 0.2 microns.

B.2.2 Exhaust Particulate Sampling System Performance

In order to function properly for sulfate emissions, the exhaust particulate sampling system should have the following capabilities:

(1) mix exhaust and diluent air rapidly,
(2) allow development of a uniform velocity profile in the flow development tunnel,
(3) minimize sampling losses in the tunnel,
(4) give equivalent emission rates with parallel filters, and
(5) maintain constant temperature at the particulate collecting stage.

All of the above have been adequately documented (1,2) and will be reviewed in this section.

B.2.2.1 Rapid Mixing of Exhaust and Diluent Air

Three methods of injecting exhaust into diluent air were tested: co-current flow, perpendicular flow, and countercurrent flow. In each case, the exhaust was injected through a 5.1 cm O.D. x 0.089 cm wall stainless steel tube into the flow development tunnel. The efficiency of the three injection methods was tested by measuring hydrocarbon concentrations in the diluted exhaust at a point approximately 2.23 m downstream of the injection point. Hydrocarbons were chosen as the tracer because they are easier to measure than particulates. If the gaseous components of the exhaust are not evenly distributed over the flow cross-section, there is no reason to believe that the particulates will be well distributed. The ultimate test of uniformity of particulate distribution in the tunnel is the consistent attainment of equivalent particulate emission rates with parallel filters. The results showed that uniform distribution was obtained only by countercurrent injection.

B.2.2.2 Development of Uniform Flow in Flow Development Tunnel

To insure that samples taken at any point in the tunnel cross-section will contain the same amount of particulate material, a uniform radial distribution of particulate material in the tunnel must be obtained. The small size of the tunnel would make it difficult to obtain reliable measurements of velocity profiles. However, it is well known that the higher the Reynolds Number of turbulent flow, the flatter the velocity profile (9). However, over the range of interest for this system, the effect of this flattening of the velocity profile is negligible. Consider the system as having a flow of air at 32°C through a 11 cm diameter pipe.

$$N_{Re} = \frac{D\overline{U}\,\rho}{\mu} \tag{1}$$

where N_{Re} = Reynolds Number

D = pipe diameter = 11.0 cm = 0.110 m

$\overline{U}$ = average fluid velocity = $\frac{4\ (13)}{\pi\ D^2}$ = 1370 m/min

8.21×10^4 m/hr.

ρ = density = 11.14 kg/m^3

μ = fluid viscosity = 0.186 cp = 0.670 kg/m-hr.

$$N_{Re} = \frac{(0.110\ \text{m})\ (8.2 \times 10^4\ \text{m/hr})\ (1.14\ \text{kg/m}^3)}{0.670\ \text{kg/m-hr}} = 154{,}000$$

Equation (1) shows that the Reynolds Number varies inversely with diameter for constant volumetric flow. Therefore, decreasing pipe diameter to 2.5 cm would increase N_{Re} to 615,000 while increasing pipe diameter to 40 cm would decrease N_{Re} to 40,000.

One measure of the flatness of the velocity profile is the ratio of the mean gas velocity to the maximum gas velocity. It has been shown experimentally that for turbulent flow in smooth pipes (9)

$$\frac{u}{U} = \left(\frac{Y}{R}\right)^{1/N} \tag{10}$$

where u = point velocity
U = maximum velocity at center
Y = distance from the wall
R = pipe radius, and
N = a constant depending on Reynolds Number

Schlicting (9) shows that average velocity $\bar{u}$ is,

$$\bar{u} = \frac{2N^2}{(N+1)\ (2N+1)} \tag{3}$$

The following table shows that the effect of changing pipe diameter over a large range would be negligible.

Effect of Reynolds Number on Velocity Profile

N_{Re}	N	$\bar{u}/U$
23,000	6.6	.807
110,000	7.0	.816
500,000	8.0	.837

Another important factor in choosing the diameter of the flow development tunnel is its effect on the length of the tunnel and the diameter of the probes. As a general rule, ten pipe diameters are usually sufficient to develop a fully turbulent velocity profile. The larger the diameter, the longer the tunnel required and the longer the residence time in the flow development section. Longer residence time leads to higher particulate settling and greater inaccuracy in the measurement. Therefore, the tunnel diameter should be minimized. However, as tunnel diameter decreases, the pressure drop through the tunnel increases and the size of the probes needed for isokinetic sampling decreases. The problems caused by high pressure drop are obvious. Smaller diameter probes should be avoided since they provide higher surface to volume ratios and result in more loss of particulate by impaction. The 11 cm diameter pipe in use offers a reasonable compromise between these various factors.

B.2.2.3 Tunnel Sampling Losses

Particulate deposition in the flow development section was measured by introducing an artifically produced mono-disperse (3.5 micron diameter) methylene blue aerosol into the exhaust injector in the same manner as for auto exhaust. The system was disassembled after the run, the tunnel surface washed with methanol and the washings analyzed spectrophotometrically. The sensitivity of the method for methylene blue is in ppb range. Analysis showed that tunnel losses are small, amounting to less than 1% of the total aerosol introduced. No dye was detected in the tunnel section housing the exhaust injector. About 0.1% of the aerosol was deposited in the tunnel mid-section, and about 0.3% was deposited in the tunnel section housing the probes. Independent tests by U. S. Environmental Protection Agency workers with a tunnel of similar dimensions have confirmed our results regarding tunnel sampling losses (10).

B.2.2.4 Equivalent Emission Rates with Parallel Filters

Since only a small fraction of the diluted exhaust is sampled for the particulate analysis, at least two parallel probes coupled to the appropriate filters are needed to serve as internal checks on the sampling system. One method of determining whether proper sampling is achieved relies on the ratio of the weight of particulate collected (W_A) by filter A, and the volume flow rate (F_A) through probe A. This ratio should equal the corresponding ratio of these parameters for filter B and probe B, that is:

$$\frac{W_A}{F_A} = \frac{W_B}{F_B} = \frac{W_C}{F_C} = \text{etc.}$$

The particulate emission rates in grams/kilometer (g/km) should be the same for all filters in a given run since

$$\frac{g}{km} = \frac{W_A}{F_A} \frac{F_P}{\Delta km} = \frac{W_B}{F_B} \frac{F_P}{\Delta km} = \text{etc.}$$

where F_P is the volume flow rate through the tunnel and Δkm the distance in kilometers accumulated on the particular test procedure.

Excellent agreement between parallel filters has been obtained using this sampling system with conventional and catalyst-equipped vehicles operating on a variety of unleaded fuels under cyclic and state test conditions. Partial documentation of this agreement has been previously described (1,2).

B.2.2.5 Temperature Maintenance of the Particulate Collection Stage

The dehumidifier is a key component of the temperature control system, particularly since the sampling system is one in which the air/exhaust dilution ratios are low, unlike other particulate sampling systems (11, 12). This means that the relative humidity of the diluent air is a key parameter. For example, during the steep acceleration portion of the Federal Test Procedure, the exhaust volume flow rate from a vehicle equipped with a 350 CID V-8 engine may be as high as 3.4 m^3/min. This means that dilution ratio would drop below 4 in the sampling tunnel. If the relative humidity of the diluent air was high, attempts to control the filter temperature at 32°C would result in condensation of water vapor, with the associated loss of particulate matter. This is shown in Figure B-4 which depicts mixture dew point-dilution ratio dependence as a function of the relative humidity of the diluent (24°C) air.

The key role of the dehumidifier can readily be seen. If the relative humidity of the diluent air is low, e.g., below 50%, it should be possible to maintain a 32°C filter temperature without condensation occurring. It can also be readily seen that in the absence of the dehumidifier, on humid days, the dew point of the mixture would exceed 32°C at dilution ratios as high as four, so that condensation would invariably occur during the acceleration portions of the driving cycle.

Attempts to control filter temperatures by omitting the dehumidification step and chilling the diluent air would be difficult to accomplish since water condensing on the coils would feed back latent heat, decreasing the efficiency of the cooler. Continued running would probably result in the condensed water freezing on the heat exchangers, rendering them inoperative.

Figure B-5 shows a typical trace of the relative humidity of the diluted exhaust in the vicinity of the sampling probes during FTP operation with a catalyst-equipped vehicle. This trace is obtained by withdrawing a sample just above the sampling probes and filtering it prior to monitoring the humidity. Filtration is necessary in order to protect the rapidly responding humidity sensor (13).

It is evident that the relative humidity in the region of the probe closely parallels the changes in the cycle driving patterns. At no point in the driving cycle does the relative humidity at the probes reach the saturation level at 32°C. As the relative humidity is lower upstream, condensation in the tunnel upstream of the probe does not occur.

Figure B-6 shows the temperature-time trace at the filter during the above run which is a typical case. A total flow rate of about 13 m^3/min. was used. A 1.2 m long x 5 cm I.D. finned tube between the tailpipe and the exhaust injector was needed to suppress temperature spikes

FIGURE B-4

DEW POINT OF DILUTED EXHAUST VS.
AIR/EXHAUST DILUTION RATIO

At Indicated Relative Humidities
of 24°C Dilution Air

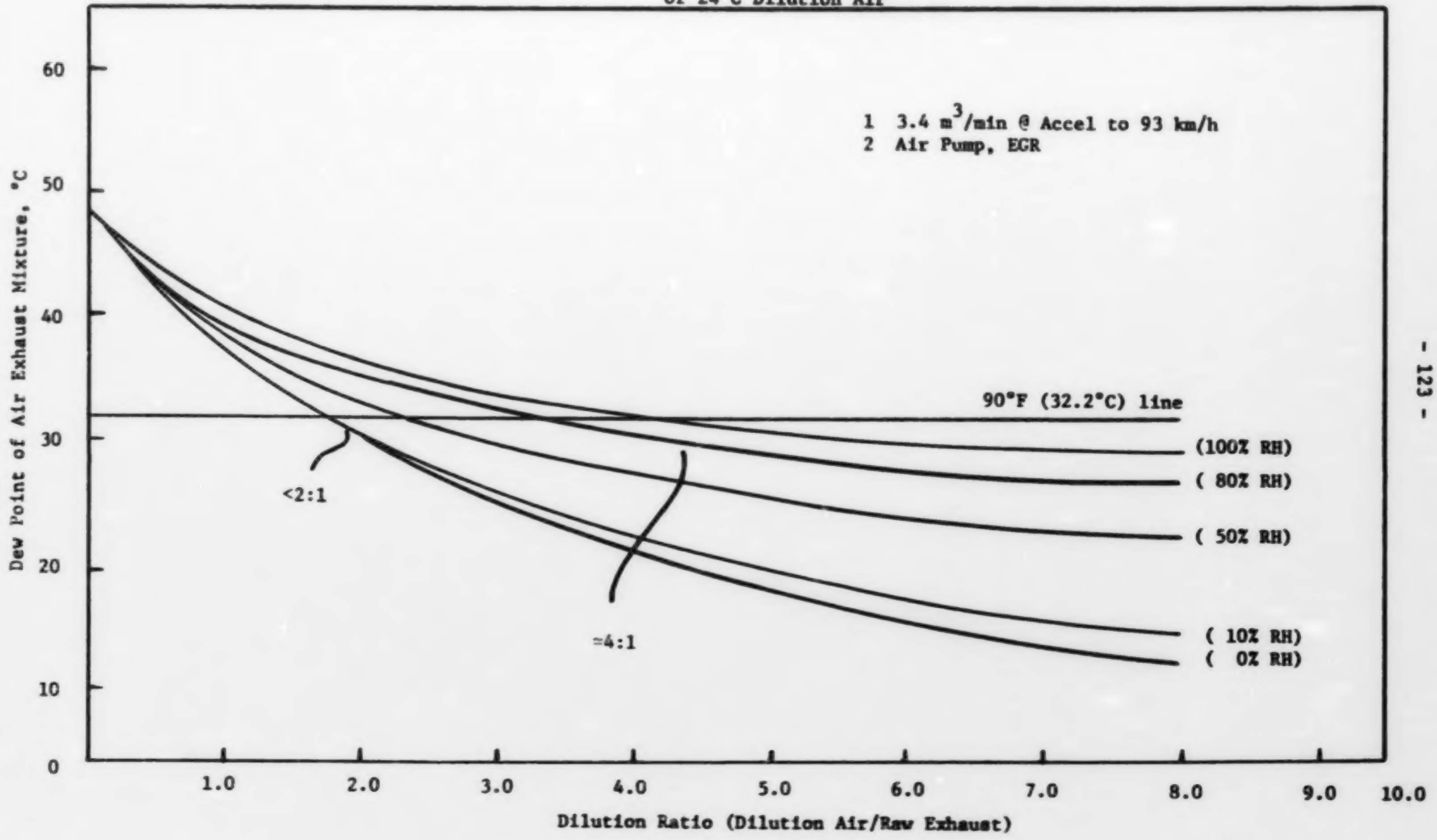


FIGURE B-5

RELATIVE HUMIDITY OF EXHAUST DILUTION AIR MIXTURE AT VICINITY OF SAMPLING PROBES DURING THE 1972 FEDERAL TEST—DRIVING CYCLE

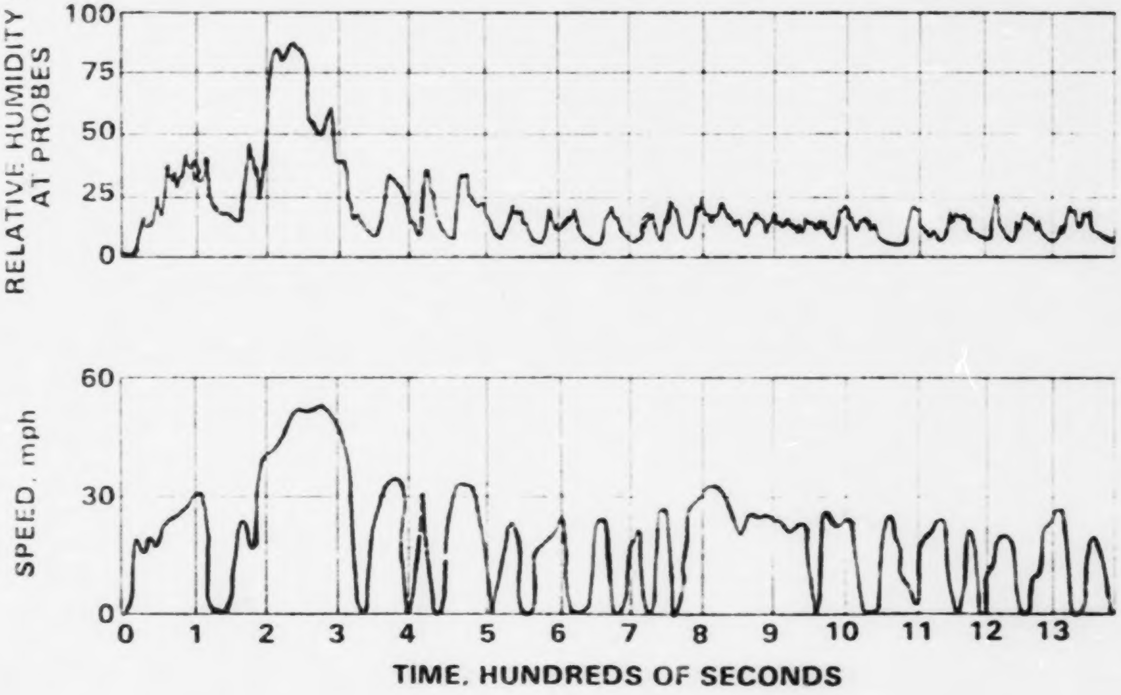
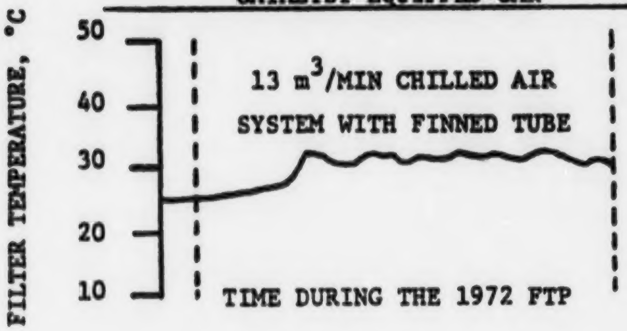


FIGURE B-6

TEMPERATURE CONTROL SYSTEM PERFORMANCE - CATALYST-EQUIPPED CAR



above 32°C during the steep acceleration portion of the driving cycle. It should be noted that the system is designed to prevent temperature excursions above 32°C, not to maintain that temperature during the course of the entire run.

Figure B-7 is a typical relative humidity-time trace for a 64 km/h steady state cruise experiment. The relative humidity surges to about 25% on start up and slowly decreases with running time.

Complete temperature control can be obtained at 64 km/h encapsulating the finned tube in a 10 cm diameter metal cylinder through which ambient air is pumped in a countercurrent direction to the flow of raw exhaust. Figure B-8 shows a schematic of this additional temperature control feature. Encapsulating the finned tube is not necessary for the driving cycle. At the 64 km/h cruise, however, the temperature would slowly rise above 32°C after about 20 minutes if the finned tube was not encapsulated.

B.2.3 The Goksøyr-Ross Technique

This technique (14) involves passing a sample of exhaust through a condenser maintained between 60 and 90°C. This is above the dew point of the H_2O in the exhaust, but below the dew point of the H_2SO_4 in the exhaust. As a result, H_2SO_4 is condensed in the coil, but H_2O which might catch SO_2, is not condensed.

In our configuration, a modified 300 mm Graham Condenser, equipped with a 60 mm diameter medium porosity fritted glass filter, is used. This unit has been found to give better than 95% collection efficiency at flow rates up to 4 liters/min. Precautions must be taken, however, with regard to the temperature of the incoming gas. If it is too hot, the coil will not provide sufficient cooling to condense all the acid. If the gas is too cool, some may condense out upstream of the coil. The sample lines leading to the condenser must also be chosen with care, to avoid possible reaction with sulfate. Glass or quartz lines are best, but if this is impossible, and mechanical considerations demand the use of metal lines, only tubing which has been passivated by prior exposure to H_2SO_4 containing gases should be used.

After sampling, the condenser coil and glass frit are emptied and rinsed thoroughly. The total liquid is diluted to a standard volume and analyzed for sulfate by the Sulfanazo III method.

B.2.4 Analytical Determination of Sulfate

Sulfate in samples collected by either the exhaust particulate sampler or the Goksøyr-Ross technique is determined by a titrimetric procedure using a color indicator, Sulfanazo III [4,5 di-hydroxy-3, 6-bis (O-sulphaphenylazo)-27, naphthalene-disulfonic acid]. The procedure

FIGURE B-7

RELATIVE HUMIDITY OF EXHAUST DILUTION
AIR MIXTURE AT VICINITY OF SAMPLING
PROBES DURING 64 km/h CRUISE CONDITIONS
at 32°C

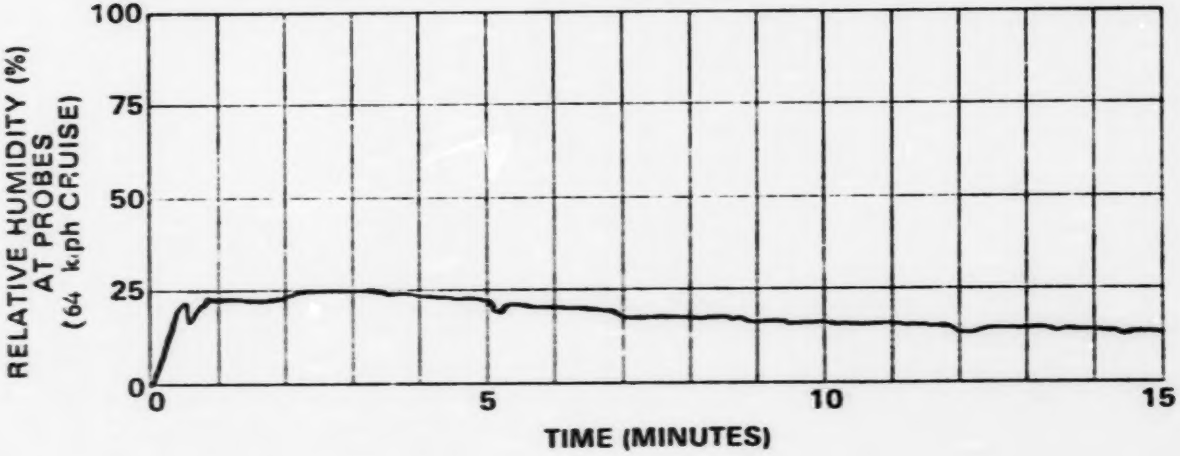
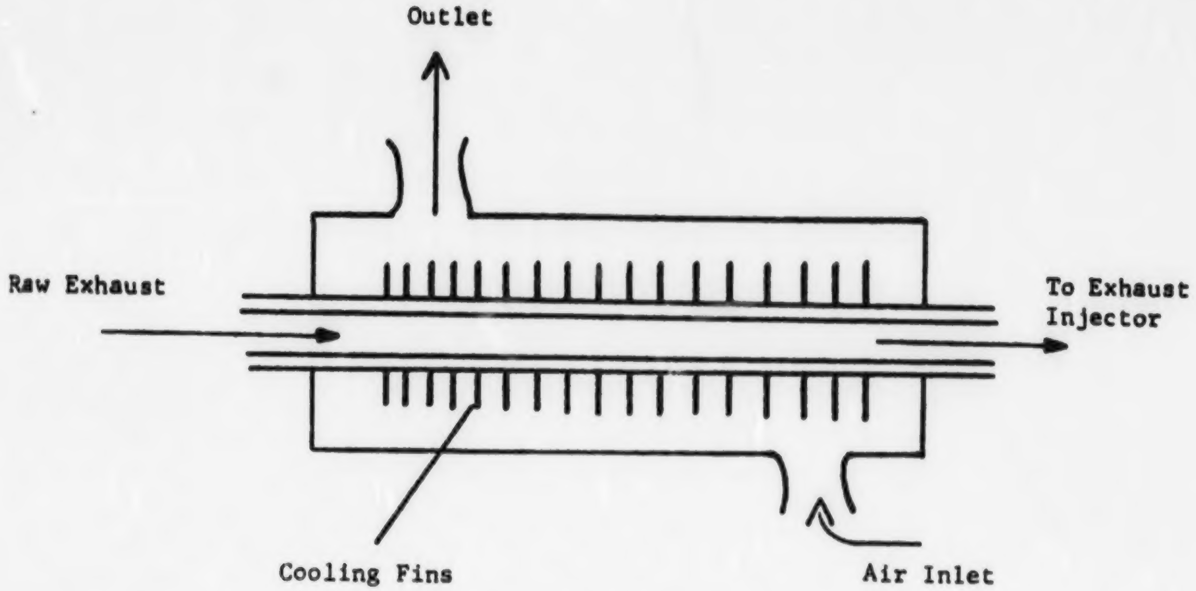


FIGURE B-8

FINNED TUBE COOLING SETUP


Outlet
Raw Exhaust
To Exhaust Injector
Cooling Fins
Air Inlet

has been adapted from that of Budesinsky and Krumlova (15).

In the case of the samples from the exhaust particulate sampler, soluble sulfate is leached from the filter with dilute nitric acid. The leach solution is heated to boiling to drive off excess nitric acid, filtered to remove insoluble material, passed through an ion-exchange column to remove interfering cations, and then buffered with methenamine to a pH of 3-4. The resulting solution is titrated with barium perchlorate using Sulfonazo (III) as the indicator. Washings from the Goksøyr-Ross coil are treated in similar fashion starting with the ion exchange step.

B.2.4.1 Reagents

The reagents used are as follows:

1. Barium perchlorate standard solution 0.01N
2. Barium perchlorate standard solution 0.001N
3. Hexamethylenetetramine (5% aqueous)
4. Sulfonazo III indicator (0.1 g/100 ml H_2O)
5. Ethyl Alcohol, absolute
6. Acetone
7. Nitric acid (2% aqueous)
8. Dowex 50 W-X8 cation exchange resin (50-100 mesh)

B.2.4.2 Titration Apparatus

The following apparatus was used in the titrations:

1. Ion exchange column, 1 cm x 25 cm.
2. Burettes (at least 0.05 ml div)
3. Low range pH paper - J. T. Baker Dual-Tint pH 1.0-4.3.

B.2.4.3 Standardization of $Ba(ClO_4)_2$ Solution

The barium perchlorate solution is standardized by titration against previously standardized 0.01N sulfuric acid as follows:

(1) 5 mls of 0.01N sulfuric acid is pipetted into a 125-ml Erlenmeyer flask.

(2) 45 mls of deionized water and 2.5 mls 2% nitric acid are added.

(3) Adjust the pH as described in the procedure and titrate with barium perchlorate solution.

(4) Calculate normality.

$$N\ Ba\ (ClO_4)_2 = \frac{\text{mls } H_2SO_4 \times N\ H_2SO_4}{\text{mls } Ba\ (ClO_4)_2}$$

B.2.4.4 Detailed Titration Procedure

(1) Cut and place 1/4 section of filter in 100-ml beaker. (1/2 filter can be used for lower levels of SO_4).

(2) Add 3.0 mls of 2% nitric acid, wetting the filter section completely.

(3) Add 20 mls of deionized water.

(4) Place small glass stirring rod in beaker and cover with watch glass.

(5) Digest samples on hot plate and allow to boil for 5 minutes.

(6) Cool beakers and filter liquid through glass wool into the ion-exchange column containing ∿7.5 g of Dowex 50 W-X8 cation exchange resin, collecting sample in 125 ml Erlenmeyer flasks.

(7) Wash beaker with 3 x 5 ml portions of deionized water. Add washings to column. After each washing, squeeze liquid from the filter by pressing it against the wall of the beaker with the stirring rod.

(8) Place the flask on a hot plate and evaporate to approximately 5 mls.

(9) Adjust the pH of the remaining solution to pH 4 using 5% hexamethylenetetramine.

(10) Add 10 mls ethyl alcohol and 25 mls acetone to the flask.

(11) Add 3 drops Sulfonazo III indicator.

(12) Titrate with 0.01N barium perchlorate solution. (If sulfate content is low, use 0.001N barium perchlorate.) If the sample requires more than 10 mls of barium perchlorate to reach the end point, the results are unreliable and should be discarded. Another portion of filter should be treated as in steps 1-7. Solution should be collected in 100 ml volumetric flask. An appropriate size aliquot is taken and the test is continued with step 8.

B.2.4.5 Effect of Nitric Acid on Measurement of Sulfate

Because nitric acid is used as the leaching agent, several experiments to ascertain the effect, if any, of nitric acid on the determination of sulfate were carried out. The test matrix, shown in the following table, shows that there is no effect of nitric acid on the titration.

Table B-1

Comparative Titrations of Sulfate of Samples With and Without Nitric Acid

Sample	Contains HNO_3	ml 0.012 N $Ba(ClO_4)_2$ to Titrate Theory	Actual	Δml
Na_2SO_4, H	Yes	5.0	4.9	-0.1
Na_2SO_4, H_2SO_4	No	5.0	4.7	-0.3
H_2SO_4	Yes	5.0	4.7	-0.2
H_2SO_4	No	5.0	4.8	-0.2

B.2.4.6 Precautions About Titration Procedure

The above procedure was arrived at after experimental work identifying sources of error and the means to minimize or eliminate these errors was worked out. Reliable results can be obtained if the following precautionary measures are taken:

(1) Keep HNO_3 at minimum
(2) Keep water in sample at minimum
(3) pH is very critical (∿4.0)
(4) Use blank for color comparison of end point
(5) Change Dowex frequently (approx. 3 samples)
(6) If sample is basic - adjust with nitric acid

For example, it was shown that not only is the ion-exchange step necessary to eliminate interference, but that it is necessary to insure that the capacity of the ion-exchange bed is not close to exhaustion. It was also shown that it is necessary to use a new batch of ion-exchange resin rather than a regenerated batch. Positive deviations were obtained when titrating the effluent from a regenerated ion-exchange bed. The results of the tests described above are shown in Table B-2.

TABLE B-2

Experiments Demonstrating Influence of Ion Exchanger on Sulfonazo III End Points

	Mls. Titration			
Mls. H_2SO_4	Theory	Actual	Δml	
Blank	0.0	0.1	+0.1	
0.5	0.5	0.5	0	
0.75	0.75	0.65	-0.1	Same column for
1.00	1.00	1.0	0	all samples
1.50	1.50	1.25	-0.25	0.012 N $Ba(ClO_4)_2$
2.00	2.00	1.45	-0.55	
2.00	2.00	2.2	+0.20	New Dowex each
1.50	1.50	1.75	+0.25	sample
1.00	1.00	1.1	+0.10	0.012 N $Ba(ClO_4)_2$
Blank	0	0.15	+0.15	
0.2	2.0	2.10	+0.10	0.0012 N $Ba(ClO_4)_2$
0.5	5.0	4.95	-0.05	
0.1	1.0	1.45	+0.45	
0.8	0.8	0.80	0	
1.0	1.0	1.00	0	New Dowex
2.0	2.0	1.90	-0.10	0.012 N $Ba(ClO_4)_2$
Blank	0	0.25	+0.25	
0.1	1.0	2.10	+1.10	
0.1	1.0	2.00	+1.00	Regenerate Dowex with
0.2	2.0	2.90	+0.90	1:5 HCl
0.2	2.0	3.00	+1.00	0.0012 N $Ba(ClO_4)_2$
2.0	2.0	1.30	-0.7	
2.0	2.0	1.40	-0.6	0.012 N $Ba(ClO_4)_2$

As shown above, the Dowex ion exchanger has to be changed frequently, and that large errors result if one attempts to work with a presumably regenerated ion exchanger. Satisfactory results can be obtained if the Dowex resin is changed after every two to three determinations.

B.2.4.7 Sulfate Determinations on Glass Fiber Filters Spiked with Known Quantities of H_2SO_4

A series of filters were spiked with known quantities of H_2SO_4 using 1.000 N H_2SO_4 and a 5 µl syringe and with 0.0112 N H_2SO_4 solutions. The filters were leached with water, the leach solution worked up for analysis as discussed in Section B.2.4.4. Figure B-9 shows a plot of added sulfate versus sulfate recovered by titration. It can readily be seen that analysis of sulfate on the filters is as reliable as analysis of solutions containing known quantities of sulfate. The next step was to determine if this method is workable with filters containing actual auto exhaust since the presence of organic exhaust particulate matter on these filters could possibly introduce substances which interfere with the color change of the titrimetric procedure. To determine if such interferences existed, the procedure was then checked against the gravimetric determination of sulfate on parallel filters from actual vehicle test runs since the presence of organic materials would have no effect on the latter determination.

B.2.4.8 Comparison of Titrimetric and Gravimetric Procedures on Filters from Vehicle Tests

Comparisons were then made between the titrimetric and gravimetric analytical procedures on particulate filters from actual vehicle runs. The titrimetric analysis was carried out on quarter sections of the filters, the gravimetric on an entire parallel filter. The particulate filters were generated from vehicles equipped with pelletized and monolithic catalysts, operating on fuels of sulfur levels ranging from 0.004 to 0.14 wt %. Both cyclic and steady state test modes were used. The results are shown in Table B-3.

Table B-3

Comparison of Titrimetric and Gravimetric $SO_4^=$ Analyses on Parallel Filters

(Actual Vehicle Runs, Sample Data)

Run Type	Fuel Sulfur, %	Catalyst Type	$SO_4^=$ Emissions, g/mi.	
			Titrimetric	Gravimetric
40 mph, 1/2 hr.	0.14	Pelletized	0.036	0.040
1975 FTP	0.065	↓	0.012	0.011
1975 FTP	0.056		0.0099	0.0081
40 mph, 1 hr.	0.004		0.004	0.004
1975 FTP	0.14	Monolith	0.306	0.287
↓	↓	↓	0.296	0.288
			0.176	0.173
	0.004		0.053	0.061
	↓		0.023	0.020
60 mph, 20 min.	0.14		0.029	0.020
↓	↓		0.259	0.239
			0.294	0.253
	0.004		0.265	0.247
	↓		0.009	0.007
			0.011	0.008
			0.011	0.008

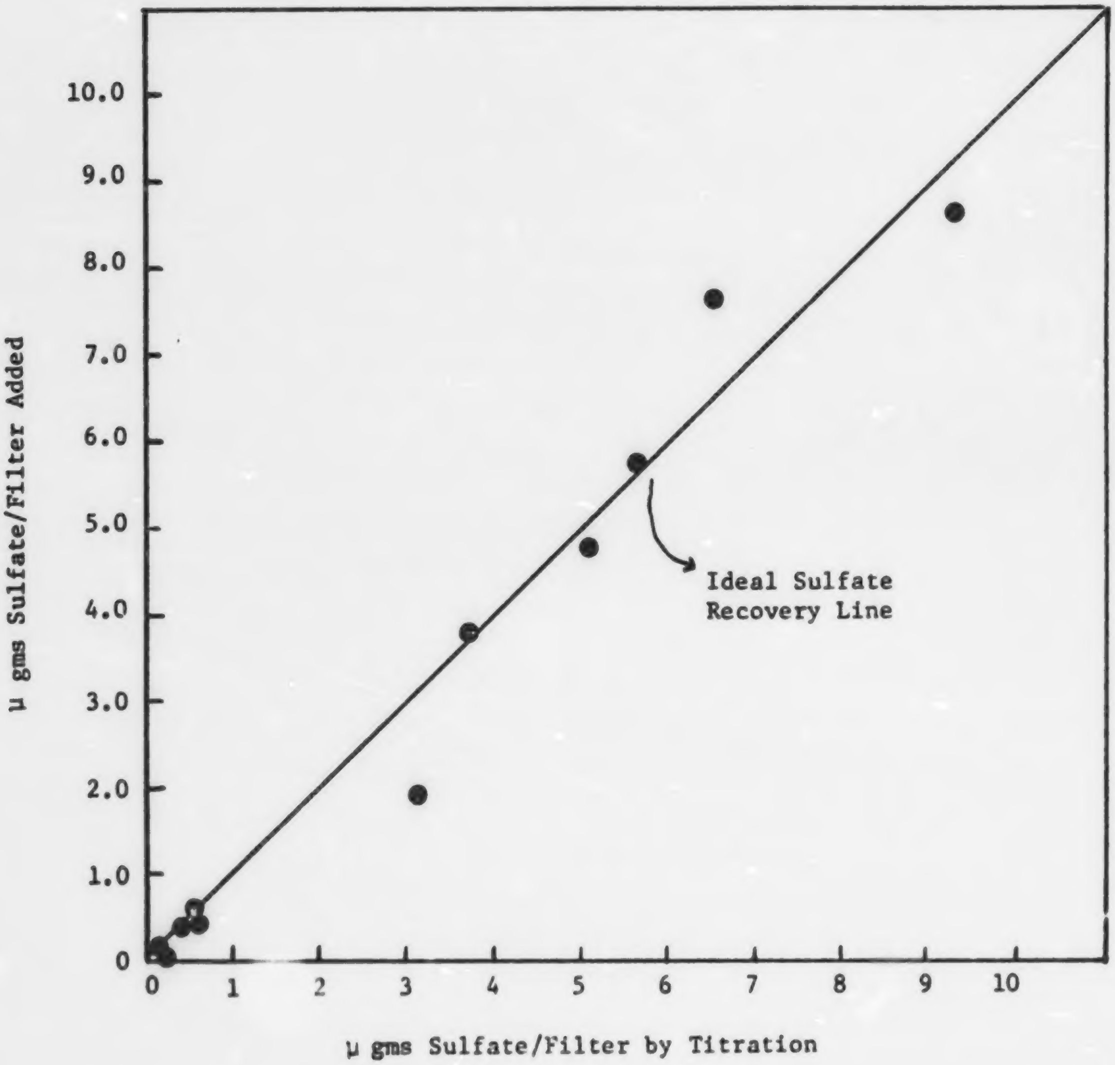
Regression analysis on 26 comparison sets showed:

$$\text{Titrimetric } SO_4^= = 1.029 \text{ Gravimetric } SO_4^= + 0.00085$$

Standard Deviation = 0.01

Figure B-9

Recovery of Sulfate From Spiked Glass Fiber Filter Samples



B.3 Measurement of SO_2 Emissions

SO_2 in diluted exhaust was measured using a Thermo Electron Corporation (TECO Model 40) Sulfur Dioxide Analyzer (16). SO_2 in raw exhaust was measured using a hydrogen peroxide bubbler method. Each of these techniques is described below.

B.3.1 The TECO Sulfur Dioxide Analyzer

This device operates on a pulsed-fluorescence UV absorption principle as follows. A gas sample is submitted to a source of pulsed ultraviolet light through a monochromatic filter. Sulfur dioxide molecules energized to an excited state by the high intensity light source, return to the ground state by emitting a monochromatic light, which passes through a narrow-band filter, and impinges upon the light sensitive surface of a photomultiplier tube. The intensity of the radiation is directly proportional to the SO_2 concentration.

This measurement method was chosen because of the following reasons:

(1) It is more convenient than wet chemical, conductimetric, or coulometric methods.

(2) Both continuous and integrated measurements of SO_2 in diluted exhaust can be made.

(3) Measurement of SO_2 emission rates could be incorporated as part of the gaseous emission measurements routinely obtained using diluted exhaust collected by the CVS system.

The operating principle of the TECO analyzer is depicted schematically in Figure B-10.

To eliminate the possibility of water adsorbing and condensing in the sample chamber on the walls and optical filters, the water in the sample stream was removed upstream to the TECO analyzer. Initially, Drierite was used to remove the water but it was found that at the 5 to 10 ppm level of SO_2, the Drierite removed all the SO_2.

The water removal problem was solved by using the Permatube Drying System (17) shown in Figure B-11. This system dries the sample stream by passing it through a bundle of tubes which are permeable to water but essentially impermeable to SO_2. Water is purged by countercurrent flow of dry air or nitrogen. The effectiveness of the permeable system in reducing the water level of a humid sample stream below 10 ppm H_2O while retaining the SO_2 in the sample has been established by our Analytical Division. The Model PD-500-72 Perma Pure Dryer according to the manufacturer (17) has the capability of taking a feed having a 50°C dew point and extracting sufficient water at 150 litres/hr. feed rate to reduce the dew point of the effluent to -30°C.

Figure B-10 Principle of Operation TECO SO_2 Instrument

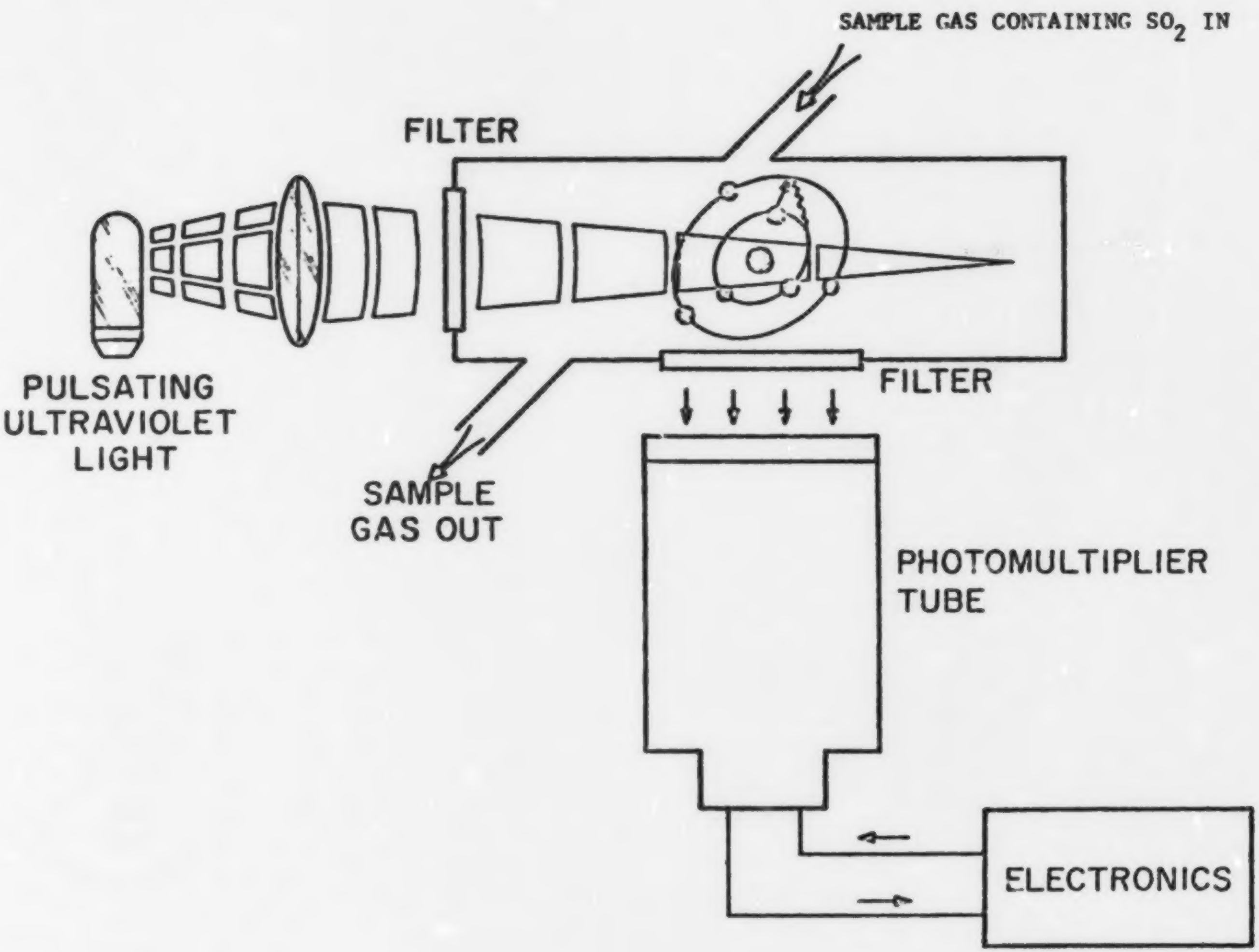
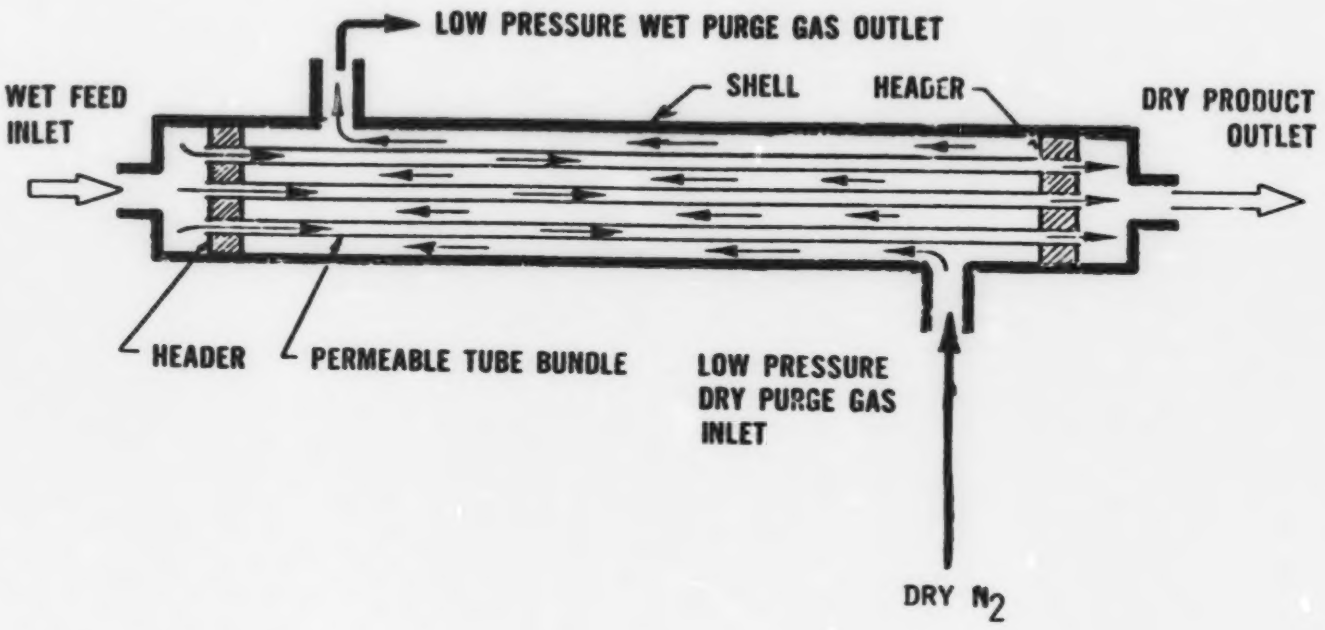

SAMPLE GAS CONTAINING SO_2 IN
FILTER
PULSATING ULTRAVIOLET LIGHT
SAMPLE GAS OUT
FILTER
PHOTOMULTIPLIER TUBE
ELECTRONICS

Figure B-11

Permatube Drying System


LOW PRESSURE WET PURGE GAS OUTLET
WET FEED INLET
SHELL
HEADER
DRY PRODUCT OUTLET
HEADER
PERMEABLE TUBE BUNDLE
LOW PRESSURE DRY PURGE GAS INLET
DRY N2

Our own tests with dry SO_2 in N_2 and in air have shown that no differences in TECO readings were obtained when the sample is introduced directly into the analyzer, or when it passes through the dryer prior to entry into the analyzer.

A millipore filter is used upstream to the dryer to prevent any particulate matter from entering and eventually clogging the dryer, and for that matter, from possibly entering and contaminating the analyzer.

It has been found that CO_2, CO, and O_2 are strong quenching agents, while N_2 exhibits a negligible quenching effect. The instrument reponse is therefore sensitive to background gas composition. Absolute values of SO_2 concentrations necessitate calibration of the instrument in a background representative of the sample to be analyzed. For example, prior to a laboratory study on SO_2 conversion as a function of oxygen concentration, it was necessary to assess the effect of oxygen quenching (18). Various samples were made by preparing bell jar mixtures containing 30 ppm SO_2, 12% CO_2, varied amounts of oxygen, and nitrogen as the balance gas. Measurements of the SO_2 concentration of these mixtures indicate an approximate 1 ppm reduction in instrument SO_2 response for each 2% increment in oxygen concentration, as shown below.

Table B-4

SO_2 Measurements at Indicated Oxygen Concentrations(a)

Oxygen Concentration (%)	TECO SO_2 Response (ppm)
0	29.7
1	28.8
2	28.4
4	26.8
6	26.2

(a) Basic Mixture, 30 ppm SO_2, 12% CO_2, balance N_2.

The quenching effects of CO and CO_2 was also measured using mixtures of 30 ppm SO_2 in pure CO and CO_2. In CO_2, the response to 30 ppm of SO_2 was 1.7 ppm, that in CO only 8.5. Measurements were then carried out on bell jar mixtures of 30 ppm of SO_2 in background air containing different concentrations of CO, O_2, C_3H_8, and CO_2. The results given below show that instrument response is sensitive to overall concentration of quenching species. Therefore data obtained where the total background concentration of quenching species changes significantly

Table B-5

Composite Effects of CO_2, O_2 and CO on TECO SO_2 Response

Mixture Composition	Total Quencher Species Concentration (%) $[CO_2] + [O_2] + [CO]$	Instrument Response (ppm)
30 ppm SO_2 1.42% O_2 0.09% CO 0.051% H_2 445 ppm C_3H_8 12.5% CO_2	14.0	28
30 ppm SO_2 4.78% O_2 14.3% CO_2 4.33% CO 348 ppm C_3H_8	23.4	23

from the calibration gas quencher level should be corrected for the inherent changes in instrument response.

For work with dilute exhaust, quenching effects are minor. Quenching by exhaust CO_2 and CO is negligible for a CVS air diluted sample due to dilution. Although the oxygen concentration increases with dilution, it presents a reasonably constant quench background and can be taken into account by calibration of dilute SO_2 in air mixtures. Properly used, the precision of this instrument is about 0.5 ppm SO_2.

B.3.2 The Peroxide Bubbler Method

In this technique the gas sample is first passed through an appropriate filter to remove any sulfate, then into a bubbler containing 80 ml. of a 3% H_2O_2 solution. The H_2O_2 oxidizes SO_2 to H_2SO_4, which is retained in the bubbler. The bubbler solution and washings are analyzed for sulfate using the Sulfanazo III technique.

B.4 References Used Appendix B

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APPENDIX C

PRACTICAL OPERATING CONSIDERATIONS WITH SULFATE AND SO_2 ANALYTICAL METHODS

C.1 Cross-Checks of Analytical Techniques

A number of analytical techniques, described in Appendix B, have been used in connection with this contract. Four basic methods are involved, as shown in Table C-1. Since there are two methods each for sulfate and for SO_2 measurement, a number of attempts were made to cross-check between the two. Some of these attempts yielded satisfactory results, while others did not. In attempting to understand the reasons behind the failures, limitations in the capabilities of some of these techniques under certain operating conditions were uncovered. These will be discussed in the following sections.

Table C-1

Characteristics of Analytical Methods

Species	Method	Exhaust Gas	Driving Modes	Sample Source
Sulfate	Filter	diluted	cyclic, constant speed	flowing gas
	Goksøyr-Ross	undiluted	constant speed	flowing gas
SO_2	TECO	diluted	cyclic, constant speed	flowing gas, bag
	Bubbler	undiluted	constant speed	flowing gas

C.1.1 Cross-Checks of Sulfate Analytical Techniques

C.1.1.1 Comparison of Goksøyr-Ross and Filter Methods

During the durability testing of sulfate traps, it was decided that a more accurate measure of trap pick-up efficiency should be obtainable by directly measuring the concentration of sulfate in the exhaust gas entering the trap during a test and comparing this to the outlet concentration determined by the particulate filter. Prior to this we had relied on periodic checks of the test vehicle, using the particulate filter, with the sorbent removed, to establish a base line for sulfate emissions from the catalyst. As our sophistication grew in the area of sulfate production over catalysts, the magnitudes of run-to-run variations and catalyst aging effects on sulfate production became apparent, prompting the desire for simultaneous measurement of trap inlet and outlet sulfate concentrations during efficiency tests.

The immediate stimulus for this type of check occurred at the beginning of the CaCO3 sorbent vehicle durability test, Section VI.2.3. Prior to mounting the trap, the vehicle, with fresh monolithic catalysts, was run for 3 200 km to age the catalysts. At this point, two one hour 64 km/h cruise runs were made, as shown in Table C-2, and values of 0.026 and 0.032 g/km of sulfate obtained on the particulate filter. This pointed up the difficulty of obtaining accurate percentage pick-up values for any given run, unless simultaneous pre-trap readings were also obtained. Therefore, subsequent readings, with the trap in place, were made of the pre-trap

Table C-2

Comparison of Goksøyr-Ross and Filter Sulfate Measurements (Pre-Trap or With Trap Removed)

64 km/h Runs

Catalyst Age, km	Sulfate Emissions, g/km Goksøyr-Ross*	Filter
3 200**	---	0.026
	---	.032
7 200	0.019	---
	.020	---
14 500	.015	---
	.023	---
20 600	.018	---
	.022	---
20 600**	.046	.036
	.045	.042
	.037	.031
	.055	.031

* pre-trap readings
** trap removed from vehicle

sulfate concentration by the Goksøyr-Ross technique, in addition to the post-trap filter measurements.

It was found that the Goksøyr-Ross readings, out to 20 600 km, were lower than the values obtained at 3 200 km by the filter method. While catalyst aging might be the reason, the Goksøyr-Ross readings showed no downward trend over this interval. At 20 600 km (corresponding to 17 400 km of trap aging) the durability test was ended, the sorbent removed from the trap canister and some mechanical repairs made to the test vehicle's engine. At this point, the vehicle, minus trap, was now used to run some direct comparisons between the Goksøyr-Ross and Filter techniques. The former samples the raw exhaust downstream of the catalyst, the latter, of course, the diluted exhaust from the particulate sampler tunnel.

Several inconsistencies were noted. First, the Goksøyr-Ross values jumped sharply from their previous levels; the four one hour cruises in this configuration averaging 0.046 g/km compared to the first six runs beginning at 7 200 km, which averaged only 0.020 g/km. It is difficult to see how removal of the trap, located downstream of the sampling point, or minor mechanical repairs, could have produced a real change in sulfate production over the catalyst of this magnitude. Experimental error involving the Goksøyr-Ross method itself may have been involved, and this will be discussed in more detail shortly.

This jump in Goksøyr-Ross readings also brought them to a level exceeding the simultaneous values determined by the filter method. The four filter values at 20 600 km averaged 0.035 g/km. In contrast, the six Goksøyr-Ross readings in the interval from 7 200 to 20 600 km had been lower than the 3 200 km values recorded by the filter, 0.020 g/km compared to 0.029.

The average filter readings at 3 200 and 20 600 km are fairly close to each other and can probably be accounted for by the known variability of catalyst vehicle sulfate emissions. However, the more than doubling of the Goksøyr-Ross readings suggests there may be some inherent sources of experimental error in the method. Our experience with this technique indicates several possible problem areas. In our runs, it was necessary to use a stainless steel tube to connect the exhaust system and the condenser itself. This line was externally heated in an effort to prevent acid condensation. However, it is difficult to balance this heating so that line condensation is completely eliminated on the one hand and the gas is not heated so high that H_2SO_4 cannot be completely condensed in the coil on the other hand. Compounding this problem is the possibility of chemical reaction on the walls of the metal sample line. Depending on the degree of sulfation of the metal surface, there may be times when reaction occurs, leading to a lower collection of acid in the coil. At other times, there may be a transfer of sulfated material from the sample line to the coil, leading to erroneously high values. The transferred material may be either entrained or revaporized acid, or else actual chunks of metal sulfate flaked off the wall.

Because of the foregoing uncertainties, additional work will be necessary to pin down and eliminate potential trouble spots in using the Goksøyr-Ross method for sampling vehicular exhaust and to ensure that it can be used reliably for this purpose. Laboratory use of this technique is much simpler and should not be subject to the same degree of uncertainty.

C.1.1.2 Comparison of Sulfate Sampling Points

The previous section described how, in the only direct simultaneous sulfate readings taken (at 20 600 km), the Goksøyr-Ross method, sampled from raw gas in the vehicle exhaust system itself, gave higher readings than the filter, sampled many feet further downstream, from the dilution tunnel. In order to ensure that this result was not due to loss of sulfate during its passage through the exhaust system and dilution tunnel, an experiment was run using a vehicle equipped with monolith oxidation catalysts but no sulfate trap. Two samples of undiluted exhaust were withdrawn simultaneously from a position equivalent to where the trap inlet would have been located and from a point just before the entrance to the dilution tunnel. These two samples were passed through the Goksøyr-Ross coil. A third sample was taken at the same time in the conventional manner by filter from the dilution tunnel. Table C-3 shows the results obtained for two successive hour readings, running the car at 64 km/hr cruise.

Table C-3

Simultaneous Sulfate Readings at Three Sampling Points

Method	Sample Location	Sulfate Emissions, g/km 1st Hour	2nd Hour
Goksøyr-Ross	inlet to empty trap	0.027	0.034
Goksøyr-Ross	inlet to dilution tunnel	.010	.014
Particulate Filter	dilution tunnel	.026	.035

Several points are of interest. First, the Goksøyr-Ross readings from the two different sampling points are not in agreement. The readings from further downstream are lower. However, it cannot be inferred from this that sulfate was lost to the walls during its passage down the exhaust system, since the filter values, still further downstream, are in excellent agreement with the first set of Goksøyr-Ross readings. A more likely explanation for the low Goksøyr-Ross readings at the dilution tunnel inlet is related to the connection to the condenser. Closer coupling of the condenser coil and the exhaust line were possible at this point. Therefore, the sample of exhaust gas may have entered the condenser at too high a temperature to permit complete capture of the acid. Unfortunately, a second condenser was not placed in series with the first to determine if this was actually occurring.

A second interesting aspect is the showing that in each of the three sampling regions, the second hour of running produced higher levels of sulfate. Referring back to Table C-2 also, it can be seen that in many cases the second of two successive one hour cruises gives higher sulfate values, and in no case is the second hour significantly lower than the first. It is possible that during the first hour of operation, the sulfate storage capacity of the catalysts were partially or completely saturated so that during the second hour emissions were more nearly equal to SO_2 oxidation.

C.1.1.3 Comparison of Absolute Accuracy of Analytical Methods

As has been seen in the two preceding sections, a number of discrepancies have been observed between simultaneous Goksøyr-Ross and filter samples, and even between simultaneous Goksøyr-Ross samples taken from different portions of the exhaust system. Although a number of possible difficulties have been pointed out which make one suspicious of the Goksøyr-Ross results, it would be desirable to have known sulfate concentrations in the exhaust gas, so that the analytical results can be compared on an absolute basis. Unfortunately, this cannot be done when the catalyst is used as the source of sulfate. Even though the $SO2$ inlet concentration to the catalyst is known from the fuel sulfur content and consumption rate, the conversion rate to sulfate is not.

In an effort to provide a known level of sulfate in the exhaust gas, a test vehicle was fitted with fresh catalysts to prevent the possibility of sulfate release from the catalyst. The car was run with essentially sulfur free fuel, <20 ppm. Sulfate was added to the system by continuously metering into the exhaust stream, just downstream of the catalysts, a known amount of 1N H_2SO_4. However, it appears that the acid was not evaporated by the hot exhaust gas rapidly enough to prevent reaction with the walls of the exhaust system. In all cases, both the Goksøyr-Ross and filter samples gave values much lower than the amount of sulfate injected. Only one result was as high as 75%, the rest ranged from about 20 to 50% recovery. Even more indicative of wall reaction was the collapse of the exhaust pipe in a cloud of orange colored smoke after only about eight hours of acid injection. Clearly then, in order to conduct a meaningful experiment of this type, an aerosol generator will have to be used rather than simple acid injection.

C.1.2 Cross-Checks of SO_2 Analytical Techniques

Two methods of measuring SO_2 have been used; the TECO pulsed UV fluorescence instrument and the H_2O_2 bubbler technique. Both are described in Appendix B. The TECO was used to sample gases from the dilution tunnel, while the bubbler could be used for both raw and diluted gases. In the former mode it was useful only for steady speed runs, with proportionally diluted gases it was possible to measure SO_2 during cyclic and steady speed runs. In the following sections, we will discuss the agreement or lack thereof between the two methods, and probable reasons for those cases where agreement was not obtained. In the case of Task 2, where non-catalyst vehicles were run, problems associated with obtaining good sulfur balances will also be discussed. Sulfur balances, of course, are not to be expected with catalyst cars because of the sulfur storage phenomenon.

C.1.2.1 TECO Results

In Appendix B, Section B.3.1., the TECO instrument and certain calibration problems were described. These problems, which basically are due to the quenching effect of CO, CO_2 and O_2 on the fluorescence of UV-excited SO_2, and to the fluorescence of hydrocarbon compounds, were not known at the beginning of our work on Task 2. The literature available on the TECO did not mention these phenomena. As a result, the TECO SO_2 values taken for the 1974 Chevrolet, Mazda, and Honda, shown in Appendix Tables E-1 through E-3, were made with an instrument calibrated using an SO_2 in nitrogen gas. This, of course, did not correct for the quenching and fluorescence interferences. An attempt was made to develop a correction factor to account for the difference in composition between the calibration gas and the air-diluted exhaust gas from which actual samples were taken, but this was not successful, as indicated by the "corrected" values for SO_2 which are given in Appendix Tables E-1 through E-3. They are uniformly high, and the Mazda gave the highest readings of the three cars. This may have been due to the high hydrocarbon emissions from this vehicle, much higher than from the other two cars. As mentioned, hydrocarbons are able to fluoresce and give a positive signal to the TECO instrument. The diesel tests showed a less than complete SO_2 balance, in contrast to the other three cars. In this instance, it is believed that fouling of the sample cell by the very high level of particulate matter in the exhaust led to the low SO_2 readings.

Another problem encountered with the TECO was that of sensitivity. Although the unit had a low range of 0-10 ppm, in practice it was found that this scale was too noisy to be used. It was necessary, therefore, to use the 0-50 ppm range. As a consequence, the unit could not be used under conditions of very low SO_2 concentration, as when low sulfur fuels were burned or with low speed driving modes, when the exhaust gas was diluted to a greater extent in the constant volume sampler.

In order to determine just how low in SO_2 concentration the instrument could be used, a tabulation was made of results from a number of runs from Task 3. In these cases, a proper instrument calibration was made, using SO_2 in air, which approximates the composition of diluted exhaust gas. These included fuels of 0.012 and 0.032 wt. % sulfur content, and FTP and 96 km/h cruise driving modes. Preconditioning of the catalysts prior to running was with either the turnpike or city driving cycle. As shown in Table C-4, the FTP runs generally yielded very low SO_2 levels in the diluted exhaust gas. During the driving cycle SO_2 levels frequently dipped well below 1 ppm. On the other hand, at 96 km/h cruise, the values were generally at least 2-3 ppm. Since there is no way of knowing the "correct" value of SO_2 which should be emitted from a given test, due to the unknown factors of catalyst storage and release or oxidation of exhaust gas SO_2, the reliability of each measurement was judged by its agreement with a simultaneous H_2O_2 bubbler reading. Although there can be no guarantee that either reading is correct for a given run, a close agreement is good evidence that both are correct.

It was found that the FTP runs, with their low SO_2 exhaust gas concentrations, gave very poor agreement between the TECO and bubbler methods. Ratios of bubbler to TECO values ranged from 0.06 to 1.55. On the other hand, the cruise values showed ratios ranging only from 0.88 to 1.24, with an average of 1.11. Thus, it appears likely that the TECO, when properly calibrated, yields reliable SO_2 readings at concentrations of several ppm or more. However, at somewhat lower levels the instrument does not appear useful. Of course, this conclusion is subject to the objection that at such low levels, the bubbler method may be subject to erratic results, along with or instead of the TECO. In the absence of any independent check on the accuracy and reproducibility of the bubbler method at such low values we can only rely on the difficulty of reading values as low as 1 ppm or below on a 0-50 ppm scale to conclude that the TECO, at least, should not be used in this concentration range.

Another test was made, at 96 km/h, to determine the absolute accuracy of the TECO unit. A non-catalyst vehicle was run for one hour, using a fuel containing 0.032 wt. % sulfur. The fuel consumption was determined and the total amount of sulfur burned was calculated as 4.46 grams. The TECO, calibrated with an SO_2 in air gas mixture, sampled the diluted exhaust gas continuously, and showed a sulfur usage of 4.60 grams.

TABLE C-4

COMPARISON OF TECO AND BUBBLER SO_2 RESULTS AS A FUNCTION OF SO_2 CONCENTRATION

Task 3 Results - Diluted Exhaust Gas

Fuel Sulfur, Wt. %	Test Condition	Driving Mode							
		FTP				96 km/h			
			g Sulfur/test				g Sulfur/test		
		ppm range	TECO	H_2O_2	H_2O_2/TECO	ppm range	TECO	H_2O_2	H_2O_2/TECO
0.032	Base Case (turnpike)	0.2-1.0* 0 - 0.8	0.18 0.11	0.19 0.17	1.06 1.55	3-4	7.5	8.2	1.09
0.032	Base Case (city)	0.3-1.4 0.2-0.7	0.43 0.18	0.26 0.25	0.60 1.39	3-5	6.4	7.0	1.09
0.012	Base Case (turnpike)	 0.3-0.5	---- 0.11	0.08 0.11	---- 1.00	2-3	4.0	4.4	1.10
0.012	Base Case (city)	0.1-2.0 0.2-1.3	0.30 0.18	0.02 0.00	0.06 ---	1-3	3.3	2.9	0.88
0.032	Restricted Air (turnpike)	1.1-4.0 0 -1.5	0.82 0.14	0.67 0.01	0.82 0.07	5-10	13.9	15.7	1.13
0.032	Restricted Air (city)	1.3-5.3 0.3-1.3	1.05 0.22	0.87 0.00	0.83 ----	3-10	13.8	16.9	1.22
0.032	Aged Catalyst (turnpike)	0 -0.8 0 -0.6	0.11 0.08	0.14 0.02	1.27 0.25	3-4	7.1	8.8	1.24

* Two FTP runs are initial and final in test sequence used in Task 3.

A final check was made of the absolute accuracy of the TECO, this time when sampling raw rather than diluted exhaust. In this case, a catalyst-and trap-equipped car was used, since sulfate analytical methods were also being examined, as described in Section C.1.1.1 of this Appendix. In two of the 64 km/h cruise runs, each consisting of two one hour intervals, TECO readings were taken before the catalyst, and between the catalyst and trap. The instrument had been calibrated with SO_2 in air. However, with an air pump supplying secondary air, the oxygen content of the sampled exhaust was about 6%. Our earlier work on oxygen quenching effects, described in Appendix B, Section B.3.1, had indicated that the correction factor between 6% and 20% oxygen should be very small.

As seen in Table C-5, the TECO values before the catalyst agreed very well with the amount of sulfur calculated to be liberated during fuel combustion, with the first two hours averaging only 1% high and the last two hours about 8% high. There was, of course, no way of judging the absolute accuracy of the TECO readings after the catalyst, so again reliance was placed on whether or not the results agreed with concurrent bubbler readings. Table C-5 shows ambiguous results were obtained. During the first two hours, the TECO readings did not agree with each other. This might have been attributed to changes in the catalyst storage characteristics, but the bubbler results do not show this hour-to-hour change. In addition, both TECO readings are substantially below their bubbler counterparts. The second set of readings, however, are in very good agreement with each other, both hour to hour and between the TECO and bubbler values. It should also be mentioned that an attempt

Table C-5

Determination of TECO Accuracy in Undiluted Exhaust Gas

64 km/h Cruise 0.032 Wt. % Sulfur Fuel

		Grams of Sulfur			
			TECO		Bubbler
Run	Hour	Consumed In Fuel	Before Catalyst	After Catalyst	After Catalyst
1	1	1.88	2.04	0.72	0.38
	2	1.89	1.78	.50	.36
2	1	1.83	2.02	.56	.55
	2	1.79	1.91	.54	.56

was made to monitor SO_2 in the dilution tunnel, but under this driving condition the concentration was under 1 ppm and erratic results were obtained.

C.1.2.2 Peroxide Bubbler Results

The second method for monitoring SO_2 emissions, besides the TECO instrument, is the use of peroxide-containing bubblers. This technique was described in Appendix B, Section B.3.2. Several comparisons involving the bubbler and the TECO were described in Section C.1.2.1. It was found that the bubbler method may have some problems when the total quantity of SO_2 absorbed is relatively small, as in the short duration, low concentration FTP runs shown in Table C-4. On the other hand, longer duration, higher concentration runs, such as the 96 km/h cruises of Table C-4 are, judging by the good cross-check with the TECO results, reliable. Other bubbler tests discussed in Section C.1.2.1 showed that the bubbler accurately measured total fuel sulfur content in a one hour, 96 km/h cruise with 0.032 wt. % sulfur fuel, but ambiguous cross-checks were not obtained during four one hour 64 km/h cruises, Table C-5.

Invariably, in those cases where the bubbler results could be compared directly to the amount of fuel sulfur consumed, the results have come out higher than expected. Such values were obtained with the non-catalyst cars used in Task 2 and with before catalyst samples from Tasks 3 and 4. A number of samples were rechecked, after titrimetric determinations, by analyzing retained portions of the sample solutions gravimetrically. These samples were taken during 96 km/h cruise tests of two non-catalyst cars. the 1974 Mazda and Honda used in Task 2, and from the 1975 350 CID vehicle used in Task 3. In this instance, the sample was taken before the catalyst. Table C-6 shows that both the titrimetric and gravimetric procedures gave higher sulfur values than calculated from the fuel consumption and sulfur content. Each result shown represents the average of 2-4 separate cruises. The gravimetric gave somewhat closer agreement, however, averaging 22% higher than the expected value. The titrimetric procedure averaged 37% higher. Some possible reasons for these high results, and steps taken to correct them are described in the next section. It should be pointed out here that although the gravimetric technique gave results in closer agreement with the calculated sulfur values, this method is not suitable for general use since its sensitivity is less than that of the titrimetric procedure, and it is much more time consuming.

C.1.2.3 Analytical Procedure Problems and Solutions

In the previous section, a comparison of titrimetric and gravimetric analyses of perioxide bubbler samples showed that both were

Table C-6

COMPARISON OF TITRIMETRIC AND GRAVIMETRIC ANALYSES OF PEROXIDE BUBBLER SAMPLES

96 km/h - Averages of one hour runs

Vehicle	Fuel Sulfur, Wt. %	Sulfur, grams/test Calculated	Titri-metric	Gravi-metric	Titrimetric / Calculated	Gravimetric / Calculated
Mazda	0.065	1.85	2.1	1.9	113	103
Mazda	.032	1.15	1.6	1.4	153	121
Honda	.065	1.10	1.4	1.4	127	127
Honda	.032	0.50	0.7	0.7	140	140
1975- 350 CID	.032	4.20	5.6	4.4	133	105
"	.032	4.25	5.0	4.7	118	110
"	.012	1.65	2.6	2.3	158	140
"	.012	1.55	2.6	2.1	168	136
"	.032	4.30	5.3	4.9	123	114
Average					137	122

higher than the expected results, with the titrimetric even higher than the gravimetric, by an average of about 12%. Thus, it appears that there is a systematic error in these techniques, leading to somewhat high results. This may have been related to uncontrolled blank corrections, which will be discussed shortly. First, the possible reasons for the difference between the titrimetric and gravimetric procedures will be considered.

It will be remembered that titrimetric analyses of peroxide bubbler samples also were high in comparison to properly calibrated TECO readings, Table C-4, by about 11% on average. Still another comparison of the titrimetric procedure, this time against the gravimetric, using filter sulfate samples, can also be made. For this purpose, the results in Appendix B, Table B-3 were used. There the titrimetric values average 14% higher than the gravimetric. Thus we have three independent checks in which the titrimetric procedure averaged 11-14% higher than TECO or gravimetric results. The most likely explanation for this lies in the difficulty of detecting the end point of the barium perchlorate-Sulfanazo III titration described in Appendix B, Section B.2.4. A rather subtle change in a shade of blue occurs, and when monitored by eye, a natural tendency would be to exceed the end point.

The problems leading to overly high sulfur values for both the gravimetric and the titrimetric methods may be related to blank corrections. Blank corrections may be required to account for any sulfate content in the deionized water used to prepare the peroxide bubbler solutions, to rinse out the bubblers after use (the rinsings are added to the sample), and to prepare the barium perchlorate titrant solution. Prior to the comparisons reported in the previous section, these blanks were not determined and used in a systematic manner. Subsequently, the blank correction was determined as 0.0023 mg/ml of bubbler solution. Since a total of 100 ml is used in each bubbler for the peroxide and rinse solutions, the correction to be applied is 0.00023 grams per bubbler determination. An illustrative calculation can be made to demonstrate the likelihood that a blank correction of this magnitude can affect the accuracy of a given test. If we assume that the equivalent of 2 grams of sulfur is emitted during the test, and the bubbler samples one part in 2800 of the exhaust gas (dilution tunnel flow rate of 400 SCF/min. and sample flow rate through the bubbler of 0.14 SCF/min.) then the equivalent of 0.0007 grams of sulfur is trapped in the bubbler, or about 0.0021 grams of sulfate. Thus the blank correction amounts to approximately 10% of the total determination, and if not subtracted out will lead to a result too high by this amount. The importance of the blank correction will depend, of course, on the total amount of sulfur trapped in the bubbler. In turn, this will depend on the fuel sulfur content, the driving mode, the length of sampling time, and the fraction of exhaust gas sampled. An examination of Tables C-4 through C-6 shows that a wide range of trapped sulfur is encountered in practice, leading to situations where the blank correction may be as large or larger than the sample itself to those where the blank correction is negligible. Since the titrimetric and gravimetric methods have consistently overestimated sulfur values, regardless of the amount of trapped sulfur, it appears that blank corrections, although they should be made systematically, do not provide the explanation for this overestimation.

After a systematic procedure was adopted for dealing with the blank correction, a series of 17 standard samples were submitted for analysis, scattered randomly among the working samples. These were designed to determine the accuracy and reproducibility of the titration procedure itself, divorced from any sampling considerations. A standard H_2SO_4 solution was used to prepare 100 ml samples, equivalent to bubbler samples, each containing 0.0048 grams of sulfate. Thus the blank correction amounts to about 5% of the true value. With this blank correction applied, the average value of the 14 usable results was 0.0051 grams of sulfate, about 0.0003 grams high.* However, the standard deviation was 0.0004 grams of sulfate, so the difference does not appear to be significant. It would seem then that some step in the sampling procedure may have led to the high results, or possibly systematic error in measuring fuel sulfur content or consumption. However, none of these possibilities seems likely. The flow rates during sampling were carefully monitored with wet test meters. Any sorption efficiencies of the bubblers would have led to low rather than high results. The fuel sulfur contents were checked in two ways. The fuels were blended carefully from low sulfur base stocks by addition of sulfur compounds. Then the sulfur levels were measured by X-ray fluorescence or micro-coulometry. In addition, round-robin studies with the laboratories have shown our analytical techniques for fuel sulfur content to be reliable. Finally, the fuel consumption values were determined simultaneously by weight loss of the fuel container and by the carbon balance method. Generally, the two techniques agreed within several percent. The reason for the overestimations of SO_2 values, therefore, remains unclear. Fortunately, this parameter is not of direct quantitative interest, since it serves generally only to provide a picture of the trends of sulfur storage on catalysts and on traps. As such, the accuracy already achieved seems satisfactory for this purpose. As will be discussed shortly, the principal measurement required, that of filter measurements of sulfate emissions, is not affected by the considerations discussed here in regard to peroxide bubbler samples for SO_2.

Before turning to the filter samples, a final word is in order regarding the blank correction. Subsequent to the completion of this contract, we have replaced our manual titration, visible end-point procedure with a fully automated system, including spectrophotometric end-point determination. Blank corrections recently determined by this improved procedure have been at least an order of magnitude smaller than that previously reported. It would appear, therefore, that the manual procedure blank was not due so much to actual sulfate contents of the solutions employed as to the ability of the human eye to detect an end point. That is, even in the absense of any sulfate, a finite amount of titrant was required to produce a visible change in indicator color. With the more sensitive instrumental method, this amount is much less.

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* The other 3 samples gave results too high or low by factors of 2 or more, due apparently to operator error, and were not used in the calculation of the average.

In the filter procedure for measuring sulfate emissions, Appendix B, Section B.2.1, an additional source of spurious sulfate can arise from the filter itself. Blank corrections from the solutions are generally negligible, since the sampling rate of 15 SCF/min. is over 100 times greater than that used for the bubbler. Therefore, even if only 1% conversion of SO_2 to sulfate is occurring, about the level encountered with non-catalyst vehicles, the blank correction would still be no greater a fraction of the filter sulfate sample than for the corresponding bubbler SO2 sample. Usually, however, our primary analytical concern is with catalyst vehicles which convert substantially more than 1% of the SO_2 to sulfate, further reducing the importance of the solution blank correction. The blank correction due to sulfate leached off the filter itself varies from batch to batch. However, the value of this correction has ranged from the equivalent of 0.5 mg/km to 1 mg/km for the FTP, and thus is important again only for very low emitting cars. However, once the blank for a given batch of filters is established, even this small source of error is eliminated.

APPENDIX D

SUPPLEMENTAL INFORMATION ON SULFATE TRAPS

D.1 Analyses of Used CaO/SiO_2/NaO Pellet Sorbant

Scanning electron microscopy, x-ray energy dispersive analysis, x-ray diffraction analysis, and chemical analyses for sulfate and carbonate have been carried out on a (CaO) sulfate "trap" from a catalytic exhaust operated vehicle. This characterization was made to determine the fate of sulfur in the automotive fuel and evaluate the effectiveness of the H_2SO_4 removal from the exhaust gas.

X-ray diffraction analysis provided the crystalline composition of the fresh and used material shown in Table I.

Table I

X-Ray Diffraction Analysis

(Crystalline Compounds Present)

Fresh	Used, 26,634 Miles
Calcium Oxide (CaO)	Calcium Oxide (CaO)
Calcium Silicate, hydrate ($Ca_2SiO_4.H_2O$)	Calcium Sulfate ($CaSO_4$)
Sodium Carbonate, hydrate ($Na_2CO_3.10H_2O$)	Calcium Silicate, hydrate
	Sodium Carbonate, hydrate

Density, pore volume, and carbonate content were also obtained on the samples with the following results:

	Fresh	Used
Density, grams/ml	2.70	2.77
Pore Volume, ml/gram	0.35	0.20
Carbonate, (calc. as % CO_2)	1.29	10.7

Infra-red examination (H. T. White - AID) of a fresh powdered sample showed calcium oxide, calcium silicate and a calcium-nitrogen compound (fresh material was prepared from a nitrate before calcination). Similar analysis for a used sample showed calcium sulfate, calcium carbonate and calcium oxide. A chloroform extract of the used sample indicated only a trace amount of hydrocarbon to be present.

Several samples of the used material and calcium sulfate was analyzed by both the titrimetric and gravimetric methods for sulfate ion. The titrimetric technique is applicable to low levels and/or small (milligram) size samples. The gravimetric method is best applied for 0.1 to 0.3 gram size samples where a more homogeneous sample is assured. Reasonable agreement was obtained and values obtained are found in Table II. Differences probably result from sample inhomogeneity.

Table II

Sulfate Analyses, % $SO_4^=$

Sample	Titrimetric $SO_4^=$ wt. %	Gravimetric $SO_4^=$ wt. %
CA-4 Used, 26,600 miles	43.83	39.79
CA-6 $CaSO_4$	75.23	68.41
CA-7 Fines 26,600 miles	59.77	51.04
CA-8 $CaSO_4$	71.23	65.62

To determine how the sulfuric acid mist reacted with and affected the lime in the usual 1/8 inch (3 mm) pills, two means of analysis were used. The first involved a careful scraping of two pills. The outside (about 1 mm) was separated for analysis. Similarly, a section about 3/4 of the way in was isolated. The remainder and the two other portions were analyzed for sulfate ion by the gravimetric method. Analyses are shown below:

Sample	Gravimetric $SO_4^=$ wt. %
Fresh ($CaO + SiO_2 + Na_2O$)	0.054
Used, 26,634 miles, ground homogenized pills	38.98
Outside of pills, 26,663 miles	47.84
3/4 way in pills, 26,634 miles	34.61
Center of pills, 26,634 miles	25.01

For the second method, x-ray energy analysis was used. A pill was cut in cross section and the surface was traversed in a line from one edge through the center to the other edge. This was done in the scanning electron microscope. X-ray energy analyses for sulfur and calcium were determined at selected locations across the catalyst pellet. The relative peak intensities for sulfur correlate with the gravimetric sulfate determinations. The relative sulfur content decreases going into the pellet, while calcium increases. This is shown in Table III.

Table III

Scanning Electron Microscopy: X-Ray Energy Spectrum(s)

(Relative Peak Intensities)

Sample in Cross Section, 3 mm Pill mm. in from outside, left or right	Sulfur ($SO_4^{=}$?) Rel. Peak Ht.	Calcium Rel. Peak Ht.
0.01 left (edge)	53	50
0.35 left	56	50
0.52 left	53	49
0.52 right	55	48
0.75 right	36	77
0.75 left	35	77
1.50 center	35	70

A scanning electron micrograph at 1,000X of a fresh CaO pill is compared with that of a used pill in Figure(s) 1 and 2. These show the granular, porous structure of the surface. In cross section they were similar.

Two glass fiber filters for total exhaust particulate collection from tests run with Ford 99 were examined. Filter L-478 was from a run, where no CaO trap was in operation. The H_2SO_4 emission was 0.127 gms. H_2SO_4 per mile. A total of 55.9 mgs. H_2SO_4 was collected. The second filter, 99-43, was from a trap operation (26,500 miles); 0.0007 grams H_2SO_4 per mile emission and only 0.87 mgs H_2SO_4 was collected. Figures 3 and 4 at 200X compare the no trap versus trap operation. The no trap filter, L-478, shows particulates in the 1-10 μm size range. Filter 99-43 has a small number of larger, 20-50 μm particles, probably from attrited trap material. At 1,000X in Figures 5 and 6 the glass fiber filter from the no trap run shows the glubular wetting of the fibers by the sulfuric acid. From the trap run (Figure 6) only a few ∿10 μm particles are observed. Figures 7 and 8 are x-ray energy spectrums obtained from the respective filters. The major peak, silicon, at 1.85 KEV is from the glass fibers. The sulfur peak at 2.3 KEV, in the no trap run has a relative intensity of 25. The very low sulfur from the "trap" run has a relative intensity of 6.

These micrographs and x-ray spectrums indicate the effectiveness of the sulfuric acid reduction using the trap material.

SCANNING ELECTRON MICROGRAPHS --1,000X ⊢—⊣ 10 μm

Fig. 1 - Fresh CaO

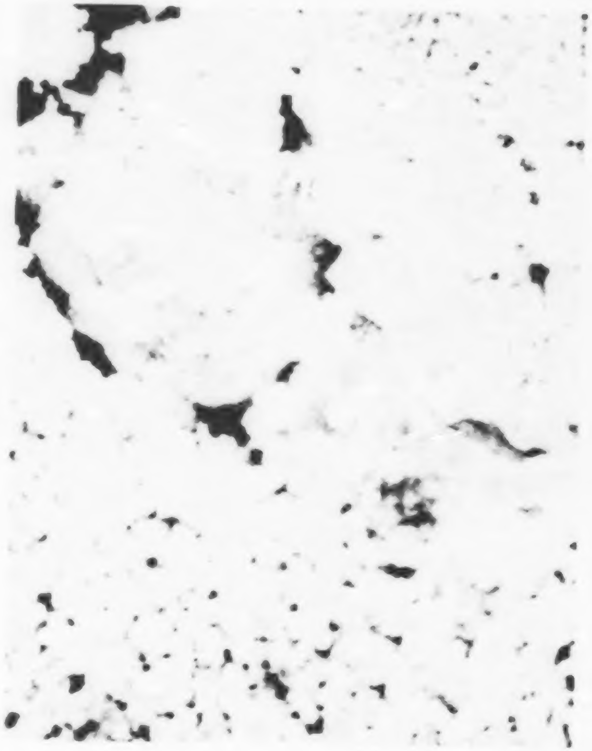
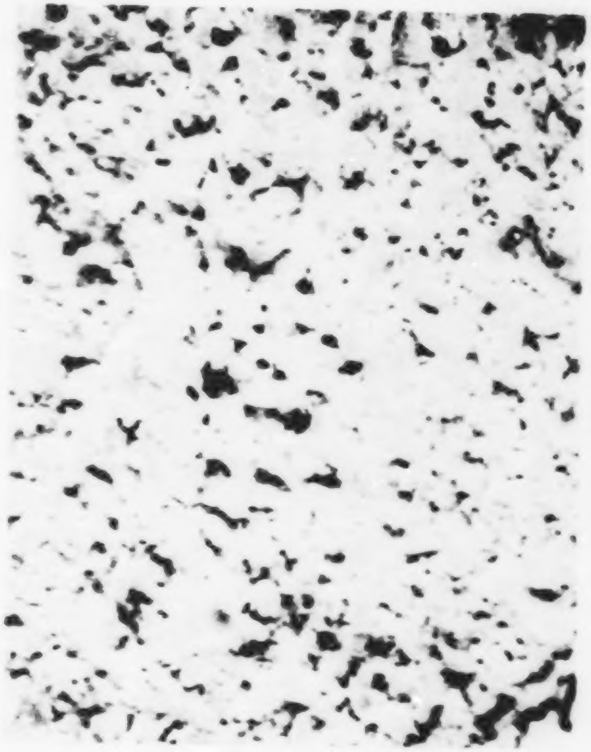


Fig. 2 - Used CaO



SCANNING ELECTRON MICROGRAPHS -- 200X ⊢⊣ 50 μm

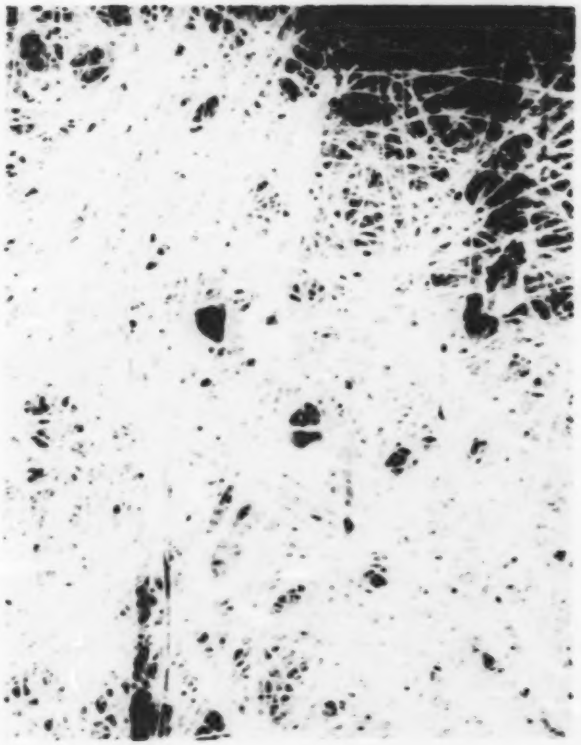
Fig. 3

L-478 No Trap

55.9 mgs. H_2SO_4
0.127 gms H_2SO_4/mile

Fig. 4

99-43 CaO Trap



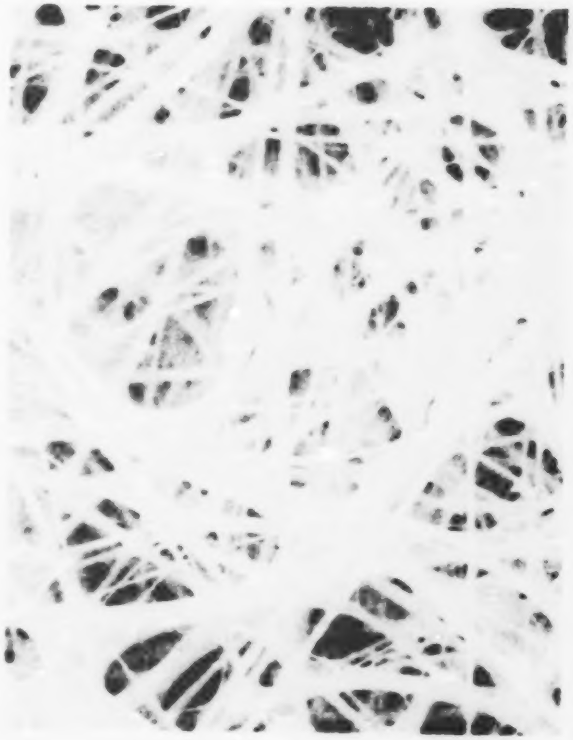
0.87 mgs. H_2SO_4
0.0007 gms. H_2SO_4/mile

SCANNING ELECTRON MICROGRAPHS -- 1,000X ⊢⊣ 10 μm

Glass Fiber Filters Ford 99

Fig. 5

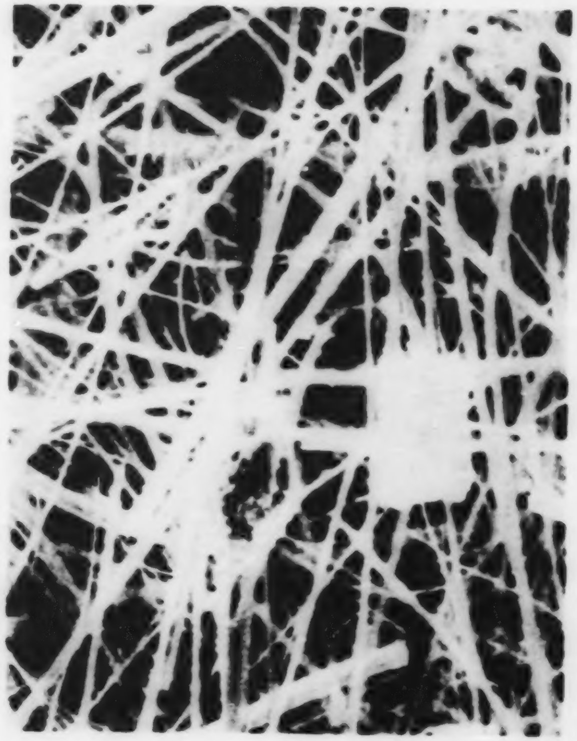
L-478 No Trap



55.9 mgs. H_2SO_4
0.127 gms H_2SO_4/mile

Fig. 6

99-43 CaO Trap



0.87 mgs. H_2SO_4
0.0007 gms H_2SO_4/mile

X-RAY ENERGY SPECTRUM(S)

GLASS FIBER FILTERS FORD 99

FIG. 7

L-478 No Trap
55.9 mgs H_2SO_4
0.127 gms H_2SO_4/mile

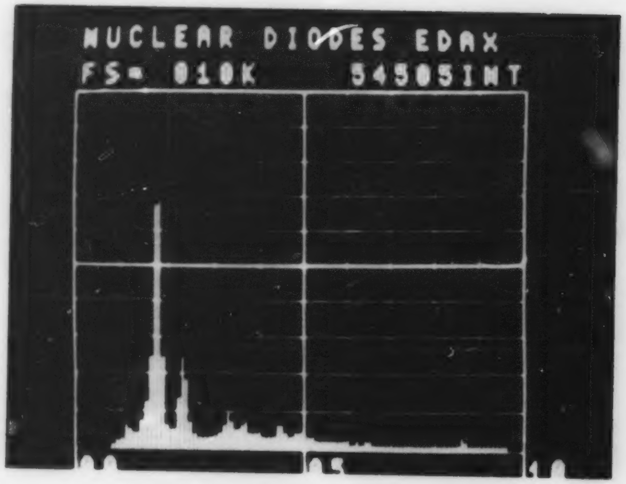
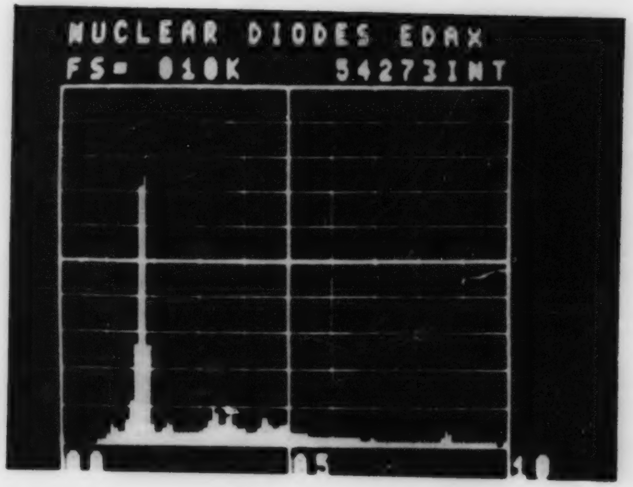


FIG. 8

99-43 CaO Trap
0.87 mgs H_2SO_4
0.0007 gms H_2SO_4/mile



Silicon, Major Peak at 1.85 KEV

Sulfur Peak at 2.3 KEV

D.2 Westvaco Corporation Report on the Use of Activated Carbon to Remove SO_3 From Exhaust

INTRODUCTION

The sulfur content of automotive fuels is converted to sulfur dioxide during combustion and is emitted through conventional engine exhaust systems in this form. However, catalytic converters which are to be installed to control hydrocarbon and carbon monoxide emissions from future automobiles have been found to cause partial oxidation of the SO_2 to SO_3. This sulfur trioxide combines with water vapor present to form H_2SO_4 which is emitted with the exhaust stream in the form of a mist or aerosol. The acid emission constitutes not only a health hazard but also could cause severe corrosion of exhaust system and body components.

Experimental evidence developed by Esso Research and Engineering indicates that the degree of SO_2 conversion to SO_3 is on the order of 30 - 70%. Since the industry average sulfur content of gasoline is 300 ppm (by weight) this translates to an exhaust stream SO_3 concentration level of about 6 - 14 ppm (by volume), or an average of 10 ppm. On this basis, acid emissions would be about 3.5 gm. 33% H_2SO_4 per gallon of fuel consumed assuming ambient conditions of 80°F and 60% relative humidity.

One possible means of control of SO_3/H_2SO_4 emissions from vehicles is the use of a reactor containing activated carbon to chemically reduce SO_3 formed in the converter back to SO_2 which is now normally emitted and which represents a less severe pollution problem. Preliminary calculations indicated that carbon consumption due to the SO_3 reaction would be only about 0.6 pound over the course of 50,000 miles under the SO_3 production conditions noted above so that such a system might well prove feasible.

The laboratory investigation discussed here was intended as a first step in establishing possible applicability of activated carbon in SO_3 control for automotive systems. Principal areas of study involved the effects of temperature and reactor space velocity on the reduction and sorption of SO_3, and the rate of side reactions with other exhaust gas constituents resulting in carbon burn-off.

EXPERIMENTAL APPARATUS

The experimental apparatus is shown schematically in Figure 1 and consisted basically of a gas mixing and SO_3 generation section, a reactor section for contacting the gases with activated carbon, a condenser and filter section for removing and collecting water and SO_3 from the effluent gas, and an SO_2 analysis section.

SO_3 and water vapor were generated simultaneously by introducing a sulfuric acid solution into a Vycor tube maintained at 1000 - 1200°F by an electric furnace. The proper liquid flow rate was obtained using a Sage Model 220 syringe pump. At the low liquid flow rate used (approximately 0.37 cc/min.) a constant rate of vapor generation was produced by admitting the liquid through a drawn glass capillary which, at its exit and in the heated zone, was in contact with a small piece of fritted Vycor glass. This arrangement was found to greatly attenuate the tendency toward vapor surges produced by the buildup and flash evaporation of individual liquid drops in the hot tube.

Other mixture gases were admitted through a concentric tube surrounding the liquid discharge capillary. Thus, flow of diluting gases through this tube prevented condensation of H_2SO_4 in the cold inlet section by preventing back diffusion of the vapor. A more detailed diagram of this inlet section is shown in Figure 2.

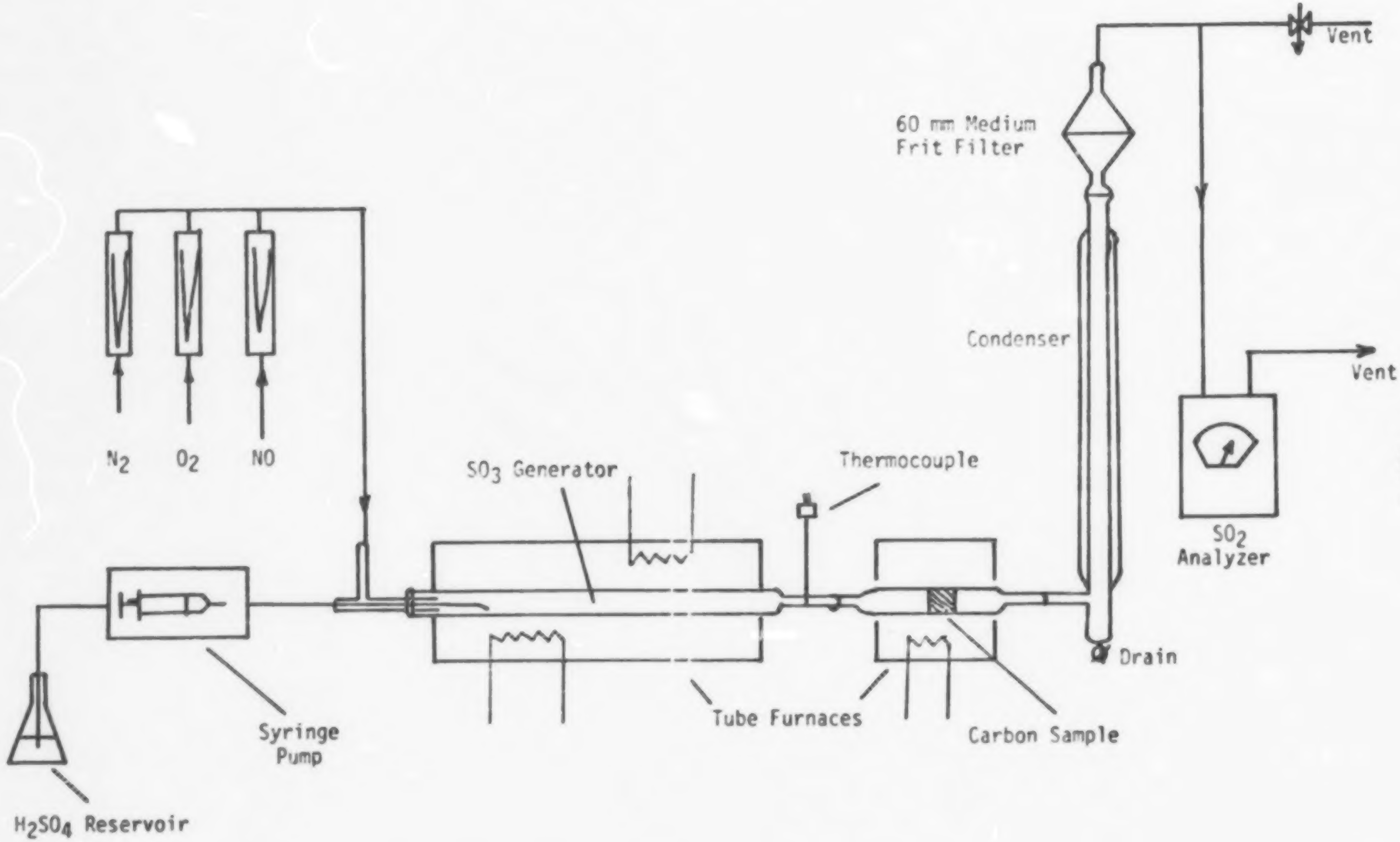
After passage through the 22 inch heated generator section the gases entered a reactor tube (0.864" ID) held in a separate tube furnace. The carbon sample was supported in this tube between a glass frit and a glass wool plug. A thermocouple inserted into the carbon bed provided temperature measurement while temperature control was performed manually using an autotransformer.

Exit gases from the reactor were conducted into a 30 inch condenser cooled by tap water. A stopcock at the bottom allowed draining of the condensate. At the top of this condenser, SO_3 not absorbed into the condensate water was trapped as H_2SO_4 mist by a 60 mm diameter medium porosity glass frit (10 - 15 micron nominal pore size).

Following this filter, SO_2 produced in the reaction with carbon was analyzed by an Envirometrics SO_2 Analyzer (Model S-364) calibrated to give full scale deflection for 10 ppm SO_2.

FIGURE 1

SO_3 REACTION APPARATUS


Vent
60 mm Medium Frit Filter
Condenser
Vent
N_2
O_2
NO
SO_3 Generator
Thermocouple
SO_2 Analyzer
Drain
Syringe Pump
Tube Furnaces
Carbon Sample
H_2SO_4 Reservoir

WESTVACO CORPORATION

Charleston Research Center N. Charleston, S. C.

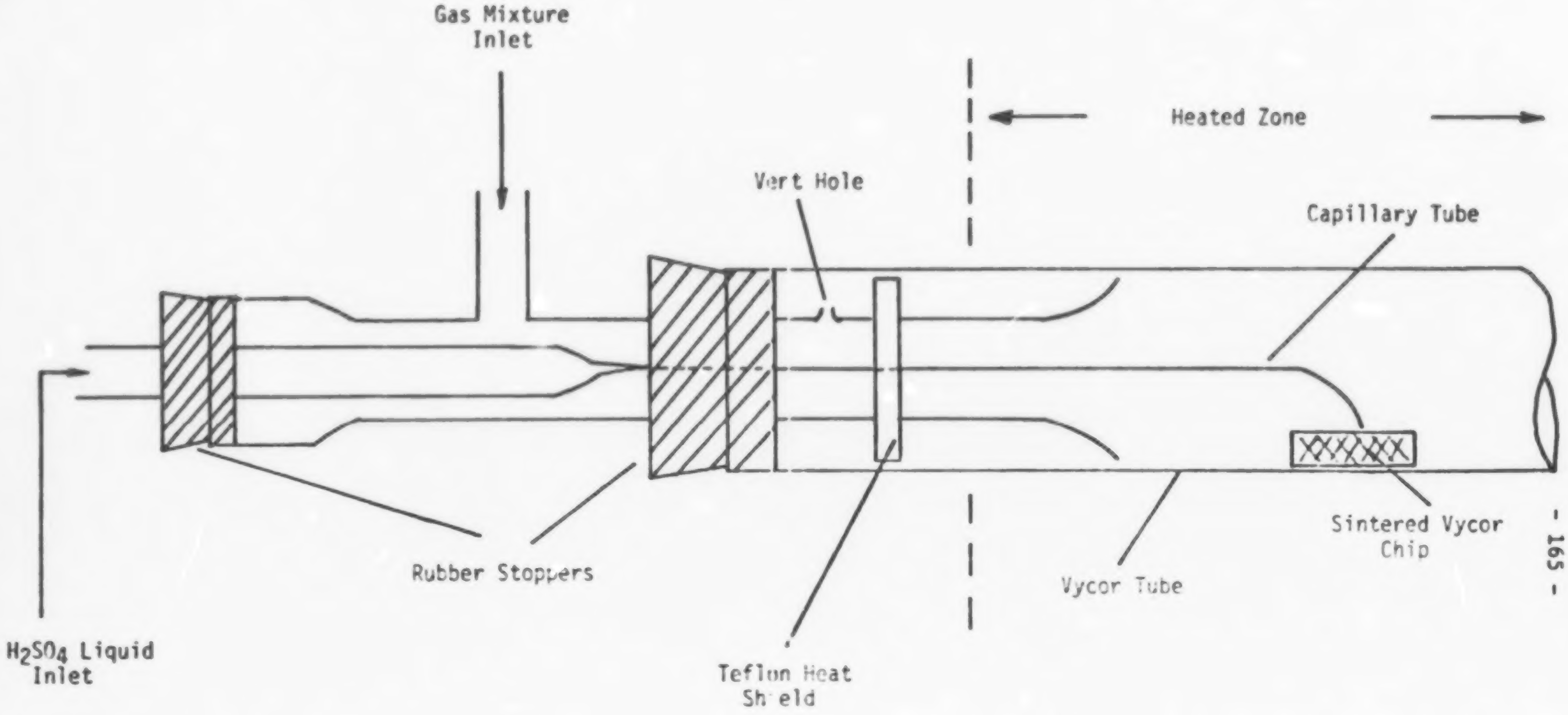

Gas Mixture Inlet
Heated Zone
Vent Hole
Capillary Tube
Rubber Stoppers
Sintered Vycor Chip
Vycor Tube
H_2SO_4 Liquid Inlet
Teflon Heat Shield

FIGURE 2. DETAIL OF GAS-LIQUID INLET TO SO_3 GENERATOR

WESTVACO CORPORATION
Charleston Research Center N. Charleston, S. C.

EXPERIMENTAL PROCEDURE

Initial tests of the apparatus were conducted without carbon in the reactor tube in order to check the SO_3 generator and test the SO_3 trap (condenser and fritted filter) for efficiency. In these "dry runs" it was indicated that the SO_3 pickup in the condenser was about equal to that filtered out by the frit, the combination giving about 85% overall recovery. Tests using an isopropanol scrubber solution following the frit indicated some leakage through this filter but a complete mass balance still could not be obtained. There were visual indications that acid mist also passed through the scrubbers without being captured. Because of these problems of incomplete SO_3 capture, the method used in later runs to establish the amount of SO_3 passing through the carbon bed was to compare the amount of SO_3 captured by the frit in the carbon reaction runs with that picked up by the frit in the dry runs (corrected for time) where there was zero conversion. Analysis of the gas stream for SO_2 showed that in fact there was no conversion in the absence of carbon in the reactor. Continuous SO_2 analyses was made during the carbon reaction studies to establish the degree conversion of SO_3.

The general procedure for carbon reaction experiments involved preheating the SO_3 generator tube to 1000°F and the carbon reactor to the desired reaction temperature under a flow of nitrogen equal to the total experimental gas flow of 10 scfm. The N_2 was then reduced to 9 cfm and the syringe pump started to inject 0.37 cc/min. of 0.01 N H_2SO_4. The SO_2 effluent concentration was monitored continuously and total SO_3 breakthrough was determined at the end of each run by washing the filter frit and titrating with 0.001 N KOH to a methyl red endpoint. Because of the very small quantities of acid involved, this titration was performed with a syringe microburet. As noted previously the ratio of the amount of SO_3 picked up on the frit to that picked up in dry runs (corrected to the same time interval) was taken as the fractional breakthrough.

EXPERIMENTAL RESULTS

Two sets of experiments were performed to investigate the SO_3 reaction with activated carbon and one series of tests was made to determine the rate of carbon burn-off in the presence of exhaust gas components.

SO_3 Reactions with 12x30 Mesh Carbon

Initial tests of SO_3 conversion were made with a 12x30 mesh (0.0661" - 0.0234") granular Westvaco carbon under the conditions outlined in Table I. The SO_3 concentration used approximates gas from catalytic converters, while the space velocity range is representative of that in reactors of practical size for automotive applications. The variables in these tests were temperature and space velocity.

TABLE I

EXPERIMENTAL TEST CONDITIONS - 12x30 MESH

Carbon Particle Size - 12x30 Mesh
Carbon Bed Depth - 1", 1/2"
Space Velocity - 30,000 - 60,000 hr.$^{-1}$ (STP)
Volumetric Flow Rate - 10 SCFH
SO_3 Concentration - 9 ppm
H_2O Concentration - 10%
N_2 Concentration - Balance
Reaction Temperature - 450°, 500°, 600°F

In each of the runs in this series it was observed that the initial level of SO_2 production was low, followed by a gradual increase toward a steady state level of conversion which was generally established within about 40 minutes.

At a reaction temperature of 600°F and a space velocity of 30,000 hr.$^{-1}$ essentially all of the influent SO_3 was reduced to SO_2 according to gas analysis. Subsequent determination of acid collected by the filter frit during the 5 hour run indicated a quantity of SO_3 equivalent to 1.4% of the influent. These results at 600°F are compared to the data obtained at 500° and 450°F in Table II.

TABLE II

RESULTS OF SO_3 REDUCTION BY 12x30 MESH CARBON

Temperature (°F)	Conversion to SO_2 (By Gas Analysis)	Total % SO_3 Removed (By Filter Analysis)
S.V. = 30,000 hr.$^{-1}$		
600 500 450	100% 80% 45%	>98% >99% >99%
S.V. = 60,000 hr.$^{-1}$		
600	94%	>98%

From these data it appears that at 600°F, the influent SO_3 was almost completely reduced to SO_2 by the carbon. At the lower temperatures, less conversion was found but since the filter titrations showed essentially complete SO_3 removal it appears that SO_3 sorption or storage took place on the carbon. Since the same carbon sample had been used in all of these runs and the experiments had been performed in the order of decreasing temperature, confirmation of the SO_3 sorption phenomenon was sought by heating the sample in a stream of nitrogen to 600°F and analyzing the effluent for SO_2. An integration of the resultant SO_2 concentration/purge volume curve accounted for about 70% of the apparently unconverted SO_3 from the 450° and 500° runs. Thus the total mass balance between SO_3 generated and SO_2 produced is close to 90% and probably within the limits of experimental error.

These data demonstrate that a high degree of SO_3 conversion to SO_2 can be obtained at a temperature of 600°F while at lower temperatures partial conversion is accompanied by almost total removal of the balance by sorption. Further, the sorbed SO_3 is shown to be reduced to SO_2 on heating to 600°F.

One additional test was made with the 12x30 mesh carbon at 600°F at a space velocity of 60,000 hr.$^{-1}$ (STP) by employing one-half the previous carbon charge in the reactor. The results indicated 94% conversion to SO_2 by gas analysis and greater than 98% removal of SO_3 as measured by filter analysis.

SO_3 Reactions with 6x8 Mesh Carbon

A second series of experiments was performed to assess the effects of temperature and space velocity on conversion using a larger mesh size carbon which may be more practical from a pressure drop standpoint in actual reactor applications.

In these runs changes in space velocity were produced by changes in bed depth at a constant feed rate. The experimental conditions are outlined as follows in Table III.

TABLE III

EXPERIMENTAL TEST CONDITIONS - 6x8 MESH

Carbon Mesh Size - 6x8 Mesh (0.132 - 0.0937")
Total Gas Flow Rate - 10 scfh
SO_3 Concentration - 9.75 ppm
H_2O Concentration - 10%
N_2 Concentration - Balance
Temperature - 600°, 550°, 500°F
Space Velocity - 23,600 to 87,500 $hr.^{-1}$ (STP)
Carbon Bed Depth - 0.33" to 1.33"

The results of these experiments are presented in Figure 3 which shows the conversion obtained as a function of space velocity and the term V/F_0 with units of

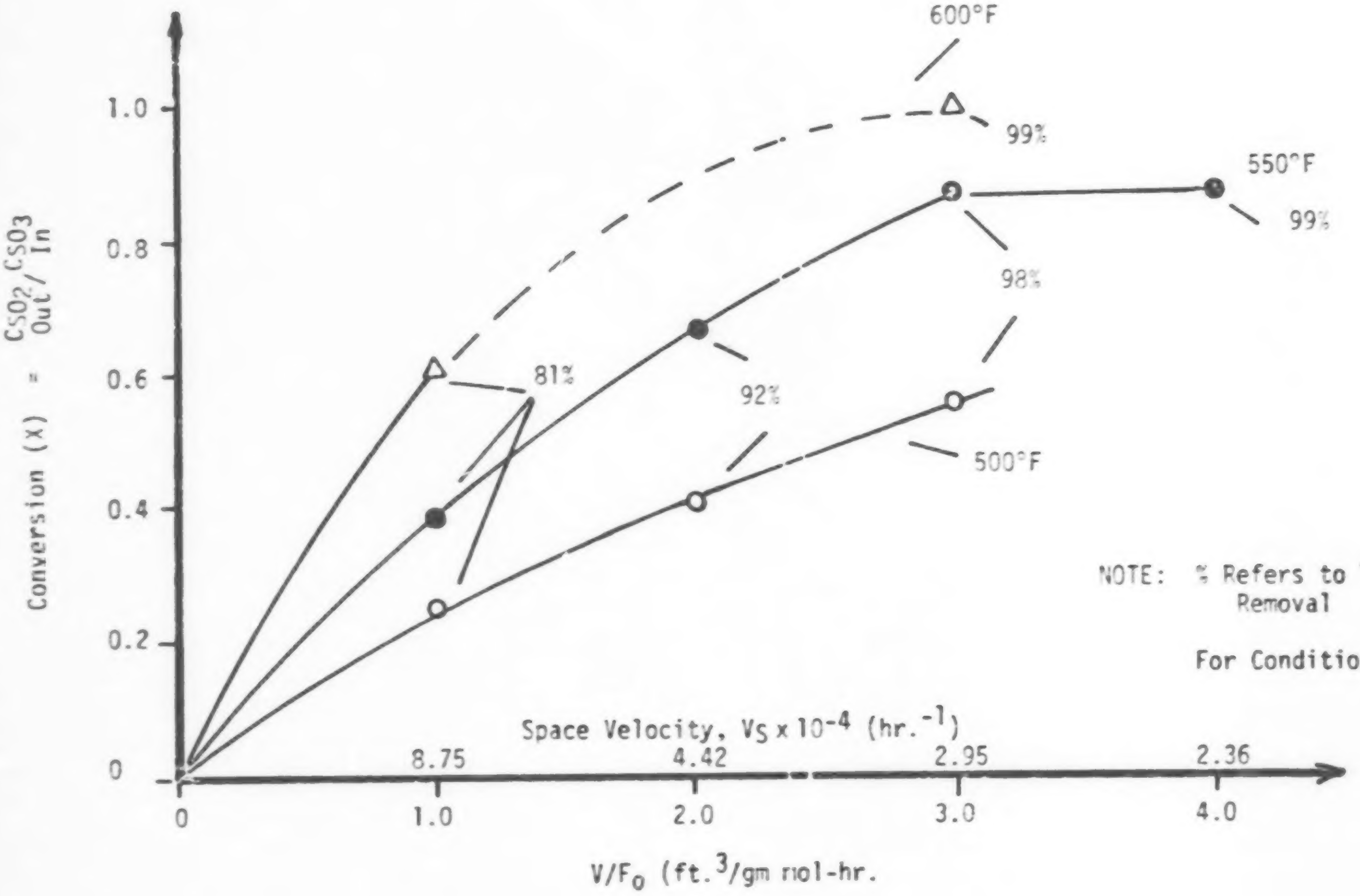
$$\text{Bed Volume (ft.}^3\text{)}/SO_3 \text{ Feed Rate (gm mole/hr.)}.$$

At a space velocity comparable to that used in the first runs with 12x30 mesh carbon (i.e. 30,000 $hr.^{-1}$) it was found that at 600°F complete conversion was again attained. At the lower temperatures, conversion was significantly less than that obtained with the smaller particle size material. As indicated by the percentage notations in this figure, total removal of SO_3 as determined by filtration was 99% at 600° and 98% for the combined runs at the two lower temperatures.

At the higher space velocities it is clear that decreases occurred in both conversion and capture of SO_3. As indicated, capture dropped to 92% for the combined runs at 44,200 $hr.^{-1}$ and 81% at 87,500 $hr.^{-1}$. It is

FIGURE 3

REDUCTION OF SO_3 TO SO_2 OVER 6x8 MESH WESTVACO GRANULAR ACTIVATED CARBON



NOTE: % Refers to Total SO_3 Removal

For Conditions See Table III

possible that SO_3 bypassing was promoted by the use of a very small reactor bed size compared to the particle size. The bed to particle diameter ratio was less than 8:1 while the bed depth to particle diameter ratio ranged down to 2:1. It is, therefore, likely that improved performance would be obtained in full size reactors.

Burn-off Tests

As noted previously the rate of carbon burn-off due to direct reaction with SO_3 is relatively small. However, reaction with other exhaust stream constituents such as O_2, H_2O and NO is also expected to contribute to carbon loss. A series of experiments was, therefore, conducted to evaluate the carbon burn-off rate due to these components.

After initial unsuccessful efforts to measure CO_2 and CO produced in the oxidation reactions, a gravimetric method was developed to determine burn-off rates. Using the same apparatus as that employed in SO_3 conversion studies, a carbon sample was simply contacted with selected gas mixtures at a space velocity of 30,000 hr.$^{-1}$ for a period of time long enough to produce a measurable weight loss. The general procedure was as follows:

1. Heat sample under N_2 purge to 700°F for 1 hour in reactor tube.
2. Cool and transfer sample to weighing tube.
3. Heat sample in weighing tube to 220°F under N_2 purge, cool under N_2.
4. Seal tube and weigh sample.
5. Transfer sample to reactor; heat to desired reaction temperature under N_2; react carbon with desired gas mixture.
6. Heat to 700° under N_2 purge.
7. Cool and repeat weighing procedure.

Post-heating at 700°F and sample conditioning prior to weighing were employed to prevent sorption effects from interfering since total weight changes due to reaction were very small.

The experimental conditions used are listed in Table IV. Various reaction gas mixtures were used and each component, when present, was at the concentration noted.

TABLE IV

EXPERIMENTAL CONDITIONS FOR BURN-OFF TESTS

Carbon Mesh Size - 6x8 Mesh

Gas Concentrations, O_2 - 3%
H_2O - 10%
SO_3 - 10 ppm
NO - 2,000 ppm
N_2 - Balance

Space Velocity - 30,000

Total Gas Flow Rate - 10 scfm

Temperatures - 600°, 700°F

Data obtained in these experiments is compiled in Table V. Listed here is the reactant mixture, temperature, average weight of sample in the reactor during each run, the weight loss due to reaction, the reaction time in hours, and a burn-off rate (-r%/hr.) as calculated from:

$$-r = \frac{\text{Wt. Loss} \times 100\%}{\text{Avg. Wt.} \times \text{Time}}$$

Initial runs (1 - 4) were made with a reaction time interval of approximately 5 hours. Because of the relatively small weight change involved, subsequent runs were made over longer intervals (approximately 20 hours) in an effort to improve accuracy. Agreement between burn-off rates obtained in the long and short runs was poor and conservative assessments of carbon performance should be made using data from the longer runs.

Several observations may be made concerning the results obtained:

1. Reactant Species

   SO_3, O_2, and H_2O are seen to react with carbon individually and in combination to a significant extent at 600°F. Compare Runs 7, 8, 9 and 10. In every case the burn-off rate due to these reactants was 2 to 5 times greater than that calculated for SO_3 alone. Compare with Run (*). Nitric oxide was not tested alone, but in mixture with other gases it did not increase the burn-off rate. Compare Run 5 with 7, and Run 2 with 3.

TABLE V

DATA FROM BURN-OFF MEASUREMENTS

Run No.	Reaction Gas	Temp. (°F)	Avg. Wt. (gm)	Wt. Loss (gm)	Time (hrs.)	Burn-off Rate (-r%/hr.)
SHORT RUNS						
1	O_2	700	5.4854	0.0148	5.2	0.052
2	SO_3, H_2O, O_2	700	5.4293	0.0984	4.8	0.38
3	SO_3, H_2O, O_2, NO	700	5.3427	0.0999	5.0	0.37
4	SO_3, H_2O, O_2, NO	600	5.2879	0.0098	5.0	0.037
LONG RUNS						
5	SO_3, H_2O, O_2, NO	600	5.2216	0.1228	25.1	0.0938
6	SO_3, H_2O, O_2, NO	700	4.7607	0.7991	25.0	0.671
7	SO_3, H_2O, O_2	600	4.2974	0.1274	22.5	0.132
8	SO_3, H_2O	600	4.1973	0.0729	22.0	0.0789
9	O_2	600	4.1418	0.0380	17.5	0.0524
10	H_2O	600	4.0795	0.0302	20.0	0.037
*	SO_3 Calculated for 4.2 GM Sample, 100% Conversion					0.018
11	SO_3, H_2O, O_2	600	4.3000	0.0497	22.0	0.0525
12	SO_3, H_2O, O_2	600	5.8239	0.0625	19.7	0.055

2. Reaction Temperature

An increase in reaction temperature from 600° to 700°F increased the burn-off rate by a factor of 7 to 10. Compare Run 3 with 4, and Run 5 with 6.

3. Carbon Properties

Carbons used in Runs 11 and 12 were specially modified to improve burn-off resistance. These carbons exhibited about half the burn-off rate produced in comparable runs with untreated materials. Compare Runs 11 and 12 with Runs 6 and 8. Gas analysis made in Run 11 showed complete conversion of SO_3 to SO_2.

CONCLUSIONS

The bench scale data that have been obtained indicate that activated carbon can be employed to chemically reduce SO_3 back to SO_2 with essentially 100% efficiency under concentration and space velocity conditions compatible with automotive applications.

At low temperatures, SO_3 is completely picked up by carbon by a sorption mechanism, with conversion to SO_2 increasing with temperature and approaching 100% at about 600°F. SO_3 sorbed at lower temperatures is evolved as SO_2 at temperatures near 600°F.

At this time the major problem area in the practical application of carbon reactors to SO_3 control appears to be that actual exhaust system temperatures typically exceed 600°F and that at temperatures much above this level, side reactions of carbon with other exhaust constituents may lead to an unacceptable rate of burn-off. Figure 4, for example, shows the predicted decrease in weight with time of an initial 4 pound reactor charge, which is representative of that estimated for full scale applications. Burn-off rates were assumed to be those found experimentally at 600° and 700°F and it was also assumed that the rate of reaction depends upon the carbon weight remaining, a point which has not actually been confirmed. The time scale in this figure is not readily converted to vehicle mileage since the reaction is so slow and a large excess of reactants is present at any flow rate or engine speed. In terms of operating hours, then, Table VI compares reactor life assuming ultimate burn-off levels of 35% and 50%.

TABLE VI

PREDICTED REACTOR LIFE
3% O_2, 10% H_2O, 10 ppm SO_3

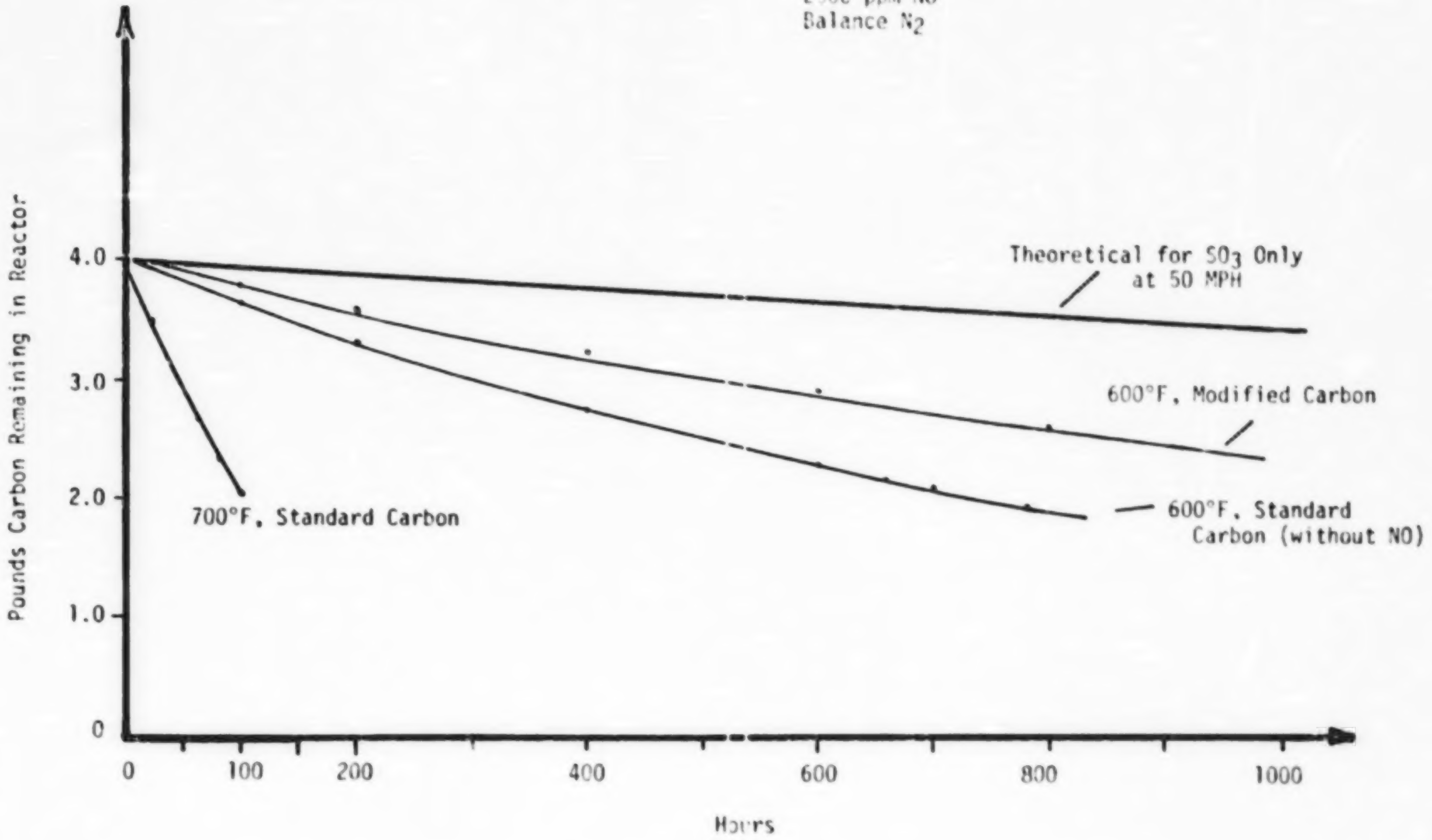
Carbon	Temperature (°F)	Rate (%/hr.)	Time to	
			35% Burn-off (hours)	50% Burn-off (hours)
Standard 6x8 M	700	0.671	60	100
Standard 6x8 M	600	0.0938	460	750
Modified 6x8 M	600	0.0550	815	1,260

From these data it is quite clear that reactor operation must be restricted to temperatures near 600°F and is likely to require special oxidation resistant activated carbon.

FIGURE 4

PREDICTED BURN-OFF OF 4 POUND CHARGE

Gas Composition: 10 ppm SO_3
10% H_2O
2000 ppm NO
Balance N_2



RECOMMENDATIONS

Laboratory results suggest that chemical reduction by activated carbon is a promising candidate technique for SO_3 emission control. Full scale prototype tests would, therefore, appear warranted unless projected reactor system costs can clearly be shown to disqualify this approach.

The reactor cost alone is expected to be low since materials of construction and fabrication would be similar to an ordinary muffler. It is further possible that this reactor might provide sufficient sound attenuation (in combination with the catalytic converter) to replace the muffler altogether, with consequent cost savings.

In terms of cost it is likely that carbon reactor feasibility may hinge on meeting the temperature control requirements which are indicated by present data. A relatively low cost control system is suggested in Figure 5. Temperature above the desired control point, acting perhaps on a bimetallic coil, would close a butterfly valve in the direct exhaust pipe and divert gases through a finned heat exchanger pipe to decrease gas temperature. Calculations could be made to estimate the required length of exchanger to maintain 600°F at the reactor.

Should prototype tests be performed Table VII lists recommended reactor configuration parameters based on conversion and pressure drop considerations.

TABLE VII

RECOMMENDED REACTOR PARAMETERS

Reactor Bed Volume - 225 - 300 in.^{2}

Wt. Carbon Charge - 4 - 5 pounds

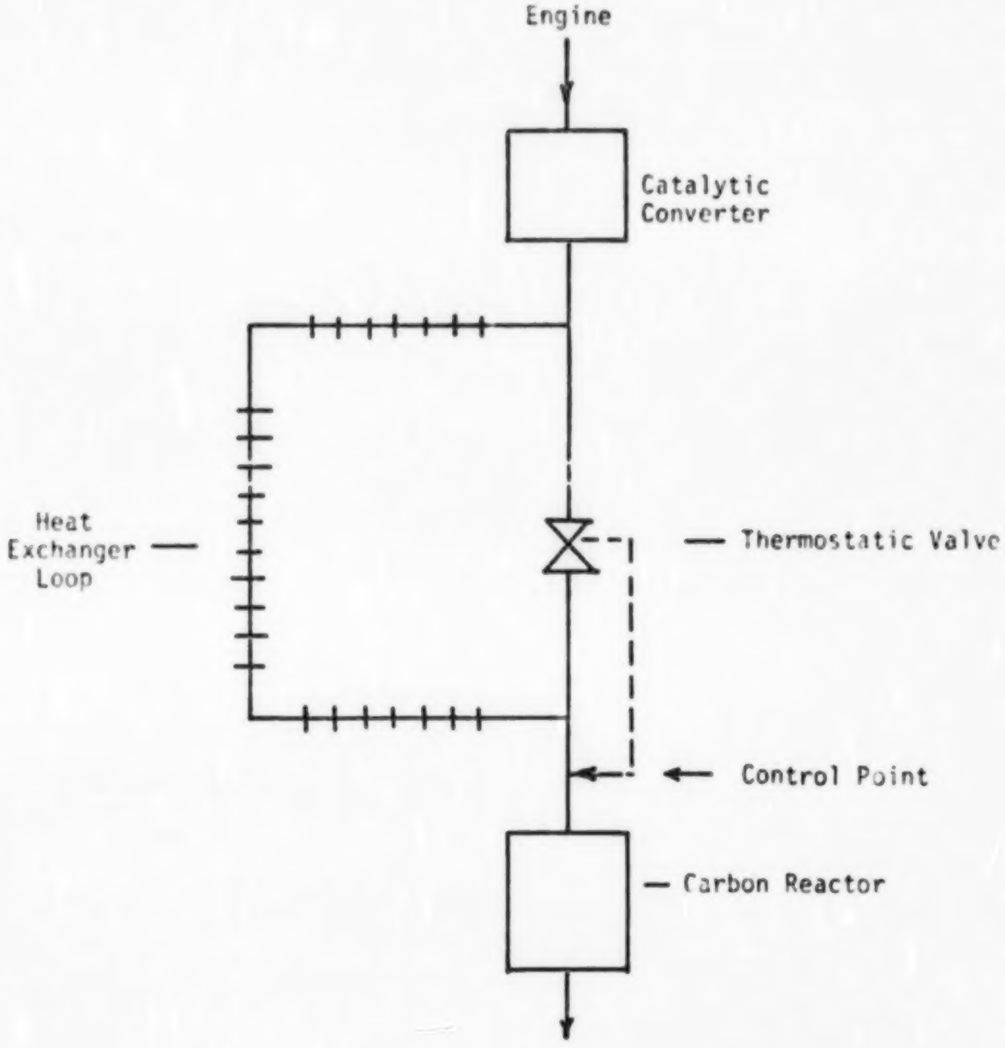
Bed Depth (D) - $1'' < D < 2.5''$

Average Bed Face Area - >120 in.^{2}

Granular C Mesh Size - 6x8 to 8x14

FIGURE 5

EXHAUST GAS TEMPERATURE CONTROLLER


Engine
Catalytic Converter
Heat Exchanger Loop
Thermostatic Valve
Control Point
Carbon Reactor

APPENDIX E

RAW DATA TABLES

TABLE E-1

EMISSIONS FROM THE 1974 CHEVROLET

Fuel Sulfur Level, Wt. %	Test Mode	Gaseous Emissions, g/km			SO2 Emissions				$SO_4^=$ Emissions			
					g/km		% of Fuel S		g/km		% of Fuel S	
		CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Raw Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Raw Exhaust	Filter, Dilute Exhaust	Gokedyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Gokedyr-Ross, Raw Exhaust
0.065	1975 FTP	7.5	0.89	1.31	0.5	-----	220	--	0.002	------	0.6	--
	20 min. idle (g/test)	37.3	4.71	4.02	2.6	0.8	220	68	0.000	<0.02	0	<1
	96 km/h (1)*	1.4	0.05	1.19	0.2	0.15	150	124	0.001	<0.002	0.5	<1
	↓ (2)	↓	↓	↓	↓	↓	↓	↓	0.002	<0.002	1	<1
	↓ (3)	↓	↓	↓	↓	↓	↓	↓	0.001	<0.002	0.5	<1
	↓ (4)	↓	↓	↓	↓	↓	↓	↓	0.001	<0.002	0.5	<1
	1975 FTP	7.1	0.88	1.31	0.3	-----	150	--	0.001	------	0.3	--
0.032	1975 FTP	7.6	0.78	0.93	0.2	-----	200	--	0.002	------	1	--
	20 min. idle (g/test)	84.6	4.40	4.10	1.6	0.4	270	68	0.033	0.05	4	5
	96 km/h (1)*	1.3	0.08	0.79	0.1	0.075	160	123	0.001	<0.002	1	<2
	↓ (2)	↓	↓	↓	↓	↓	↓	↓	0.001	<0.002	1	<2
	↓ (3)	↓	↓	↓	↓	↓	↓	↓	0.001	<0.002	1	<2
	↓ (4)	↓	↓	↓	↓	↓	↓	↓	0.001	<0.002	1	<2
	1975 FTP	7.3	0.81	1.12	0.2	-----	220	--	0.002	------	1	--

* CO, HC, NO_x, and SO_2 values given represent an average over the two hour test.

TABLE E-2

EMISSIONS FROM THE 1974 MAZDA RX-4

					SO_2 Emissions						$SO_4^=$ Emissions			
		Gaseous Emissions, g/km			g/km			% of Fuel S			g/km		% of Fuel S	
						H_2O_2 Bubbler			H_2O_2 Bubbler					
Fuel Sulfur Level, Wt. %	Test Mode	CO	HC	NO_x	TECO, Dilute Exhaust	Dilute Exhaust	Raw Exhaust	TECO, Dilute Exhaust	Dilute Exhaust	Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust
0.065	1975 FTP	18.6	2.47	0.65	0.4	0.3	---	200	150	---	0.000	------	0.0	--
	20 min. idle (g/test)	1.2	0.06	0.42	1.0	1.6	1.0	130	200	130	0.000	<0.02	0.0	<2
	96 km/h (1)*	36.5	3.32	0.32	0.4	0.14	0.13	360	119	112	0.000	<0.002	0.0	<1
	↓ (2)	↓	↓	↓	↓	↓	↓	↓	↓	↓	0.000	<0.002	0.0	<1
	(3)										0.000	<0.002	0.0	<1
	(4)										0.000	<0.002	0.0	<1
	1975 FTP	19.6	2.43	0.74	0.6	0.3	---	310	150	---	0.002	------	0.7	--
0.032	1975 FTP	18.5	2.51	0.97	0.7	0.1	---	690	100	---	0.003	------	2	--
	20 min. idle (g/test)	0.6	0.18	0.59	1.0	0.8	0.6	250	200	150	0.002	<0.02	0.2	<3
	96 km/h (1)*	15.7	7.68	0.5	0.5	---	0.097	660	---	135	0.000	<0.002	0.0	<2
	↓ (2)	↓	↓	↓	↓	↓	↓	↓	↓	↓	0.000	<0.002	0.0	<2
	(3)										0.000	<0.002	0.0	<2
	(4)										0.000	<0.002	0.0	<2
	1975 FTP	17.6	2.05	0.84	0.6	0.2	---	590	200	---	0.002	------	1	--

* CO, HC, NO_x and SO_2 values given represent an average over the two hour test.

TABLE E-3

EMISSIONS FROM THE 1974 HONDA CVCC

Fuel Sulfur Level, Wt. %	Test Mode	Gaseous Emissions, g/km			SO_2 Emissions						$SO_4^=$ Emissions			
					g/km			% of Fuel S			g/km		% of Fuel S	
						H_2O_2 Bubbler			H_2O_2 Bubbler					
		CO	HC	NO_x	TECO, Dilute Exhaust	Dilute Exhaust	Raw Exhaust	TECO, Dilute Exhaust	Dilute Exhaust	Raw Exhaust	Filter, Dilute Exhaust	Gokşøyr-Ross** Raw Exhaust	Filter, Dilute Exhaust	Gokşøyr-Ross** Raw Exhaust
0.065	1975 FTP	2.2	0.53	0.99	0.2	0.07	----	180	60	---	0.001	------	0.6	--
	20 min. idle (g/test)	5.4	2.82	0.67	0.7	0.26	0.60	180	65	150	0.000	0.063	0.0	10
	96 km/h (1)*	0.1	0.01	0.69	0.1	0.08	0.10	130	105	130	0.000	0.003	0.0	3
	↓ (2)	↓	↓	↓	↓	↓	↓	↓	↓	↓	0.000	0.003	0.0	3
	80 km/h (1)*	0.1	0.02	----	0.1	----	0.09	150	---	125	0.000	0.003	0.0	3
	↓ (2)	↓	↓		↓	----	↓	↓	---	↓	0.000	0.006	0.0	6
	1975 FTP	2.6	0.66	1.21	0.2	0.08	----	180	70	---	0.000	------	0.0	--
0.032	1975 FTP	2.3	0.60	1.41	0.1	0.05	---	180	90	---	0.000	------	0.0	--
	20 min. idle (g/test)	6.4	2.62	1.22	0.7	----	0.4	350	---	200	0.000	0.033	0.0	11
	88 km/h (1)*	0.1	0.01	0.49	0.1	0.04	0.04	290	120	120	0.000	<0.001	0.0	<2
	↓ (2)	↓	↓	↓	↓	↓	↓	↓	↓	↓	0.000	<0.001	0.0	<2
	1975 FTP	2.2	0.47	1.38	0.1	0.02	----	180	36	---	0.000		0.0	--

* CO, HC, NO_x and SO_2 values given represent averages of the one hour tests conducted.
** Spurious H_2O condition in lines.

TABLE E-4

EMISSIONS FROM THE 1974 PEUGEOT DIESEL

Fuel Sulfur Level, Wt. %	Test Mode	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions			
					g/km		% of Fuel S		g/km		% of Fuel S	
		CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross,* Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross,* Raw Exhaust
0.17	1975 FTP	2.13	0.39	0.90	0.076	0.26	25	85	0.011	---	2.4	---
	20 min. idle (g/test)	26.9	5.68	1.77	0.18	1.24	20	135	0.047	---	3.4	---
	96 km/h (1)	0.35	0.12	0.79	0.047	0.13	28	57	0.005	---	1.9	---
	↓ (2)	0.30	0.12	1.11	0.081	↓	33	↓	0.005	---	1.4	---
	↓ (3)	0.29	0.10	1.15	0.080	↓	34	↓	0.006	---	1.8	---
	↓ (4)	0.27	0.10	1.14	0.066	↓	28	↓	0.006	---	1.7	---
	1975 FTP	1.93	0.36	0.94	0.039	0.17	12	56	0.023	---	5.1	---
0.35	1975 FTP	1.93	[illegible]	0.98	0.39	0.35	60	54	0.012	---	1.2	---
	20 min. idle (g/test)	25.9	4.21	1.75	1.12	1.10	55	54	0.070	---	2.3	---
	96 km/h (1)	0.45	0.07	1.01	0.39	0.24	92	48	0.012	---	1.8	---
	↓ (2)	0.54	0.09	1.17	0.37	↓	71	↓	0.009	---	1.1	---
	↓ (3)	0.55	0.10	1.18	0.36	↓	68	↓	0.009	---	1.1	---
	↓ (4)	0.57	0.09	1.19	0.35	↓	67	↓	0.011	---	1.3	---
	1975 FTP	2.21	0.38	0.91	0.33	0.24	55	40	0.013	---	1.4	---

* Goksøyr-Ross technique could not be used with diesel because particulates in the exhaust blocked the frit.

TABLE E-5

EMISSIONS FROM THE BASE CASE PELLETED OXIDATION CATALYST SYSTEM WITH AN AIR PUMP

Fuel Sulfur Level, Wt. %	Test Mode	Gaseous Emissions, g/km			SO2 Emissions				$SO_4^=$ Emissions				Sulfur Balance, Bubbler + Filter
					g/km		% of Fuel S		g/km		% of Fuel S		
		CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Gokadyr-Rose, Raw Exhaust	Filter, Dilute Exhaust	Gokadyr-Rose, Raw Exhaust	
TURNPIKE DRIVING PRECONDITIONING													
0.032	1975 FTP	2.27	0.19	1.96	0.032	0.031	29	28	0.011	---	6.7	---	35
	20 min. idle (g/test)	0.89	1.24	3.15	0.0(a)	0.34	0	63	0.026	0.008	3.3	1.1	66
	96 km/h (1)	0.036	0.024	5.30	0.12	0.085	144	100	0.104	0.0004	84	0.3	150
	(2)	0.027	0.020	5.72	0.08	↓	94	↓	0.062		47		↓
	(3)	0.022	0.025	6.00	0.07	↓	80	↓	0.047	0.0002	37	0.1	↓
	(4)	0.029	0.019	6.06	0.05	↓	60	↓	0.038		30		↓
	1975 FTP	2.24	0.19	2.26	0.021	0.028	20	26	0.0027	---	1.7	---	28
0.012	1975 FTP	---	---	---	---	0.009	---	23	0.0015	---	4.6	---	28
	20 min. idle (g/test)	0.02	0.56	5.10	0.0(a)	0.24	0	100	0.021	0.008	5.8	2.5	106
	96 km/h (1)	0.042	0.019	5.31	0.041	0.046	122	133	0.052	0.0009	103	[illegible].8	205
	(2)	0.045	0.015	5.59	0.037	↓	107	↓	0.033		65		↓
	(3)	0.029	0.017	5.74	0.037	↓	105	↓	0.031	0.0011	59	2.1	↓
	(4)	0.042	0.019	5.71	0.051	↓	145	↓	0.033		61		↓
	1975 FTP	2.68	0.17	2.27	0.012	0.012	30	30	0.0016	---	2.7	---	33
CITY DRIVING PRECONDITIONING													
0.032	1975 FTP	2.20	0.17	2.26	0.048	0.028	47	28	0.0094	---	6.1	---	34
	20 min. idle (g/test)	0.15	0.58	5.40	0.0(a)	0.32	0	34	0.029	0.0	2.1	0.0	36
	96 km/h (1)	0.029	0.015	5.02	0.091	0.072	106	82	0.093	0.0002	72	0.2	128
	(2)	0.031	0.012	5.42	0.057	↓	64	↓	0.050		38		↓
	(3)	0.036	0.018	5.42	0.062	↓	70	↓	0.050	0.0006	38	0.5	↓
	(4)	0.021	0.019	5.58	0.050	↓	55	↓	0.047		34		↓
	1975 FTP	1.49	0.14	2.36	0.020	0.028	20	27	0.0017	---	1.1	---	28
0.012	1975 FTP	3.17	0.22	2.35	0.044	0.0033	105	8	0.0044	---	7.0	---	15
	20 min. idle (g/test)	2.72	0.10	5.43	0.26	0.11	108	47	0.015	0.008	4.0	2.5	51
	96 km/h (1)	0.039	0.018	5.44	0.057	0.030	164	91	0.050	0.0006	96	1.1	147
	(2)	0.023	0.014	4.88	0.026	↓	78	↓	0.021		41		↓
	(3)	0.021	0.020	4.85	0.026	↓	78	↓	0.023	0.0011	46	2.2	↓
	(4)	0.028	0.019	4.85	0.026	↓	78	↓	0.020		41		↓
	1975 FTP	2.11	0.16	2.08	0.023	0.0	58	0.0	0.0015	---	2.2	---	[illegible]

(a) Below detection limit.

TABLE E-6

EMISSIONS FROM THE BASE CASE MONOLITHIC OXIDATION CATALYST SYSTEM WITH AN AIR PUMP

Fuel Sulfur Level, Wt. %	Test Mode	Gaseous Emissions, g/km CO	Gaseous Emissions, g/km HC	Gaseous Emissions, g/km NO_x	SO_2 Emissions g/km TECO, Dilute Exhaust	SO_2 Emissions g/km H_2O_2 Bubbler, Dilute Exhaust	SO_2 Emissions % of Fuel S TECO, Dilute Exhaust	SO_2 Emissions % of Fuel S H_2O_2 Bubbler, Dilute Exhaust	$SO_4^{=}$ Emissions g/km Filter, Dilute Exhaust	$SO_4^{=}$ Emissions g/km Goksoyr-Ross, Raw Exhaust	$SO_4^{=}$ Emissions % of Fuel S Filter, Dilute Exhaust	$SO_4^{=}$ Emissions % of Fuel S Goksoyr-Ross, Raw Exhaust	Sulfur Balance, Bubbler + Filter
TURNPIKE DRIVING PRECONDITIONING													
0.032	1975 FTP	2.16	0.19	1.75	0.049	0.078	42	64	0.021	------	12	---	76
	20 min. idle (g/test)	0.69	0.36	5.27	0.19	0.23	25	30	0.032	0.024	2.5	2.0	32
	96 km/h (1)	0.22	0.030	5.49	0.042	SAMPLE LOST	50	SAMPLE LOST	0.060	0.0030	47	2.4	----
	↓ (2)	0.22	0.031	5.50	0.040	↓	48	↓	0.047		38		↓
	↓ (3)	0.20	0.032	5.49	0.040	↓	48	↓	0.047	0.0023	37	1.8	↓
	↓ (4)	0.20	0.031	5.64	0.040	↓	47	↓	0.047		36		↓
	1975 FTP	2.13	0.19	2.11	0.017	0.368	14	55	0.025	------	14	---	69
0.012	1975 FTP	3.55	0.24	1.79	0.016	0.048	35	104	0.011	------	17	---	121
	20 min. idle (g/test)	0.36	0.39	6.22	0.13	0.054	43	19	0.027	0.0	6.4	0.0	25
	96 km/h (1)	0.18	0.033	4.85	0.018	0.032	58	103	0.040	0.0031	83	6.5	154
	↓ (2)	0.16	0.035	5.21	0.010	↓	32	↓	0.019		40		↓
	↓ (3)	0.16	0.031	5.34	0.010	↓	32	↓	0.019	0.0022	40	4.7	↓
	↓ (4)	0.16	0.025	5.13	0.014	↓	45	↓	0.019		41		↓
	1975 FTP	4.08	0.31	1.94	0.015	0.035	35	75	0.0038	------	5.8	---	81
CITY DRIVING PRECONDITIONING													
0.032	1975 FTP	3.42	0.60	2.11	0.015	0.098	14	82	0.025	------	15	---	97
	20 min. idle (g/test)	0.11	0.37	5.71	0.13	0.054	16	7	0.037	0.027	2.9	2.2	10
	96 km/h (1)	0.23	0.039	6.07	0.044	0.062	53	73	0.057	0.0011	45	0.9	113
	↓ (2)	0.22	0.039	6.15	0.046	↓	54	↓	0.050		39		↓
	↓ (3)	0.20	0.038	5.93	0.044	↓	53	↓	0.048	0.0007	38	0.5	↓
	↓ (4)	0.20	0.035	5.44	0.046	↓	54	↓	0.050		39		↓
	1975 FTP	2.81	0.31	1.93	0.014	0.110	12	88	0.027		15		103
0.012	1975 FTP	1.16	0.17	1.91	0.028	0.043	60	93	0.0089	------	13	---	106
	20 min. idle (g/test)	0.69	0.37	6.19	0.0	0.022	0	7	0.010	0.044	2.4	10.0	9
	96 km/h (1)	0.24	0.035	5.37	0.024	0.032	72	97	0.031	0.0013	62	2.5	138
	↓ (2)	0.24	0.035	5.37	0.024	↓	72	↓	0.018		36		↓
	↓ (3)	0.24	0.035	5.51	0.016	↓	49	↓	0.016	0.0012	32	2.5	↓
	↓ (4)	0.22	0.030	5.36	0.020	↓	60	↓	0.016		32		↓
	1975 FTP	----	-----	----	0.014	0.034	34	78	0.0044	------	6.5	---	85

TABLE E-7

EMISSIONS FROM THE PELLETED OXIDATION CATALYST SYSTEM WITH LIMITED SECONDARY AIR

All Tests Conducted With 0.032 Wt. % Sulfur Fuel

Test Mode	Gaseous Emissions, g/km			SO_2 Emissions, g/km		SO_2 Emissions, % of Fuel S		$SO_4^=$ Emissions, g/km		$SO_4^=$ Emissions, % of Fuel S		Sulfur Balance, Bubbler + Filter
	CO	HC	NO_x	TECO Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	
TURNPIKE DRIVING PRECONDITIONING												
1975 FTP	2.37	0.17	2.22	0.14	0.11	130	105	0.0049	------	1.2	---	106
20 min. idle (g/test)	0.34	0.43	2.91	0.0(a)	0.0	0	0.0	0.0003	0.022	0.0	2.5	2.5
96 km/h (1)	0.045	0.022	5.05	0.21	0.16	244	178	0.057	0.0003	44	0.2	199
↓ (2)	0.086	0.019	5.33	0.16	↓	179	↓	0.021		16		↓
↓ (3)	0.016	0.020	5.77	0.10	↓	109	↓	0.016	0.0007	11	0.4	↓
↓ (4)	0.052	0.016	5.77	0.099	↓	105	↓	0.016		11		↓
1975 FTP	3.42	0.21	2.21	0.040	0.038	37	35	0.0006	------	0.4	---	35
CITY DRIVING PRECONDITIONING												
1975 FTP	3.44	0.19	1.72	0.19	0.14	197	145	0.0028	------	1.8	---	147
20 min. idle (g/test)	1.38	0.69	1.89	0.13	0.046	30	10	0.002	0.006	0.3	0.9	11
96 km/h (1)	0.030	0.010	2.14	0.15	0.175	213	257	0.038	0.0005	32	0.5	267
↓ (2)	0.37	0.007	1.57	0.16	↓	212	↓	0.006		5.8		↓
↓ (3)	6.34	0.039	1.14	0.21	↓	312	↓	0.001	0.0004	1.0	0.6	↓
↓ (4)	3.73	0.019	1.35	0.066	↓	99	↓	0.001		1.0		↓
1975 FTP	4.3	0.21	1.70	0.045	0.012	45	11	0.0010	------	0.7	---	12

(a) Below detection limit.

TABLE E-8

EMISSIONS FROM THE MONOLITHIC OXIDATION CATALYST SYSTEM WITH LIMITED SECONDARY AIR

All Tests Conducted With 0.032 Wt. % Sulfur Fuel and Turnpike Driving Preconditioning

	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions				
				g/km		% of Fuel S		g/km		% of Fuel S		
Test Mode	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Rose, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Rose, Raw Exhaust	Sulfur Balance, Bubbler + Filter
1975 FTP	4.90	0.22	1.99	0.028	0.036	24	30	0.0028	------	1.6	---	32
20 min. idle (g/test)	0.26	0.45	5.24	0.12	0.22	17	31	0.028	0.019	2.7	1.8	33
96 km/h (1)	0.71	0.066	5.06	0.066	0.088	86	118	0.0051	0.0074	4.4	6.6	121
(2)	0.30	0.055	5.06	0.054		86		0.0025		2.2		
(3)	0.29	0.054	5.06	0.060		80		0.0029	0.0024	2.6	2.2	
(4)	0.29	0.053	5.20	0.060		81		0.0043		3.9		
1975 FTP	5.73	0.33	1.92	0.125	0.133	106	107	0.0028	------	1.6	---	109

TABLE E-9

EMISSIONS FROM THE PELLETED OXIDATION CATALYST SYSTEM OPERATED AT HIGH SPACE VELOCITY (WITH AN AIR PUMP)

All Tests Conducted With 0.032 Wt. % Sulfur fuel and Turnpike Driving Preconditioning

1975 FTP	2.21	0.18	2.18	0.047	0.020	49	20	0.018	------	13	---	33
20 min. idle (g/test)	0.28	0.75	4.23	0.0	0.24	0	44	0.000	0.0	0.0	0.0	44
96 km/h (1)	0.068	0.017	6.21	0.099	0.092	116	106	0.114	0.0036	89	2.9	158
(2)	0.056	0.031	5.86	0.050		58		0.052		41		
(3)	0.056	0.012	6.21	0.040		47		0.050	0.0045	39	3.5	
(4)	0.081	0.017	6.97	0.072		79		0.055		40		
1975 FTP	1.78	0.13	2.19	0.036	0.009	37	9	0.008		5.6	---	15

TABLE E-10

EMISSIONS FROM THE MONOLITHIC OXIDATION CATALYST SYSTEM OPERATED AT LOW SPACE VELOCITY (AND WITH AN AIR PUMP)

All Tests Conducted With 0.032 Wt. % Sulfur Fuel and Turnpike Driving Preconditioning

Test Mode	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions				Sulfur Balance, Bubbler + Filter
				g/km		% of Fuel S		g/km		% of Fuel S		
	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	
1975 FTP	1.29	0.10	2.21	0.031	0.112	28	101	0.017	------	10.4	---	111
20 min. idle (g/test)	0.24	0.19	15.1	0.00	0.06	0	7	0.20	0.032	15	2.4	22
96 km/h (1)	0.018	0.011	5.39	0.017	0.040	24	57	0.080	0.0055	77	5.3	109
↓ (2)	0.041	0.006	5.69	0.008	↓	12	↓	0.050		47		↓
(3)	0.018	0.007	5.84	0.010		14		0.047	0.0065	44	6.1	
(4)	0.018	0.006	5.62	0.017		23		0.044		41		
1975 FTP	1.70	0.16	2.14	0.014	0.048	13	44	0.013	------	8.1	---	52

TABLE E-11

EMISSIONS FROM THE PELLETED OXIDATION CATALYST SYSTEM OPERATED AT HIGH SPACE VELOCITY WITH A Pt CATALYST (AND AN AIR PUMP)

Test Mode	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Sulfur Balance, Bubbler + Filter
1975 FTP	2.20	0.11	1.93	0.048	0.016	49	17	0.034	------	23	---	40
20 min. idle (g/test)	0.27	0.34	3.23	0.12	0.0	22	0.0	0.0018	0.0	0.2	0.0	0.2
96 km/h (1)	0.050	0.011	5.89	0.14	0.114	166	143	0.150	0.0016	125	1.1	207
↓ (2)	0.056	0.011	6.03	0.076	↓	96	↓	0.059		50		↓
(3)	0.044	0.012	5.89	0.070		88		0.049	0.0008	41	0.6	
(4)	0.050	0.015	5.89	0.070		88		0.049		41		
1975 FTP	2.60	0.15	1.79	0.025	0.018	25	18	0.007	------	4.4	---	22

TABLE E-12

EMISSIONS FROM THE MONOLITHIC OXIDATION CATALYST SYSTEM WITH Pt CATALYSTS (AND AN AIR PUMP)

All Tests Conducted With 0.032 Wt. % Sulfur Fuel and Turnpike Driving Preconditioning

	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions				
				g/km		% of Fuel S		g/km		% of Fuel S		
Test Mode	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Ross, Raw Exhaust	Sulfur Balance, Bubbler + Filter
1975 FTP	1.60	0.19	1.58	0.030	0.040	27	34	0.024	------	14	---	48
20 min. idle (g/test)	0.43	0.13	5.27	0.12	0.23	15	29	0.20	0.023	16	2.0	45
96 km/h (1)	0.080	0.010	3.63	0.016	0.043	21	57	0.051	0.0019	45	1.7	94
(2)	0.080	0.009	3.98	0.010		13		0.038		34		
(3)	0.075	0.015	3.84	0.016		21		0.042	0.0019	37	1.7	
(4)	0.068	0.004	3.63	0.002		28		0.038		33		
1975 FTP	2.08	0.17	1.46	0.014	0.044	12	39	0.042	------	25	---	64

TABLE E-13

EMISSIONS FROM THE PELLETED OXIDATION CATALYST SYSTEM OPERATED AT HIGHER THAN NORMAL TEMPERATURE (AND WITH AN AIR PUMP)

1975 FTP	2.93	0.11	1.53	0.083	0.045	79	41	0.010	------	6.3	---	47
20 min. idle (g/test)	0.27	0.34	2.87	0.0	0.011	0	1.3	0.000	0.0	0.0	0.0	1.3
96 km/h (1)	0.025	0.006	3.76	0.099	0.102	119	120	0.098	0.0013	78	1.0	163
(2)	0.030	0.000	3.90	0.078		91		0.046		36		
(3)	0.022	0.006	4.11	0.076		90		0.039	0.0011	30	1.0	
(4)	0.019	0.002	3.90	0.058		67		0.036		28		
1975 FTP	0.98	0.068	1.44	0.037	0.004	35	3.7	0.0047	------	2.9	---	6.6

TABLE E-14

EMISSIONS FROM THE MONOLITHIC OXIDATION CATALYST SYSTEM OPERATED AT LOWER THAN NORMAL TEMPERATURE (AND WITH AN AIR PUMP)

All Tests Conducted With 0.032 Wt. % Sulfur Fuel and Turnpike Driving Preconditioning

	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions				
				g/km		% of Fuel S		g/km		% of Fuel S		
Test Mode	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Gokcedyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Gokcedyr-Ross, Raw Exhaust	Sulfur Balance, Bubbler + Filter
1975 FTP	4.57	0.36	1.89	0.099	0.089	85	73	0.0068	------	3.8	---	77
20 min. idle (g/test)	3.45	0.72	11.4	0.70	0.44	81	51	0.037	0.014	2.8	0.9	54
96 km/h (1)	0.24	0.036	5.44	0.032	0.029	40	37	0.064	0.0068	54	5.9	84
↓ (2)	0.24	0.036	5.38	0.030	↓	39	↓	0.055		48		↓
(3)	0.21	0.033	5.51	0.030		38		0.044	0.0039	38	3.1	
(4)	0.24	0.033	5.79	0.036		46		0.055		47		
1975 FTP	3.11	0.28	2.08	0.077	0.090	67	75	0.014	------	8.3	---	83

TABLE E-15

EMISSIONS FROM THE PELLETED OXIDATION CATALYST SYSTEM OPERATED WITH HIGH METAL LOADING CATALYST (AND AN AIR PUMP)

1975 FTP	2.34	0.20	2.36	0.045	0.015	47	15	0.012	------	12.0	---	27
20 min. idle (g/test)	0.04	0.24	4.74	0.0	0.26	0	46	0.012	0.0	1.4	0.0	47
96 km/h (1)	0.031	0.010	6.05	0.090	0.072	114	91	0.104	0.0021	88	1.7	146
↓ (2)	0.025	0.020	5.90	0.076	↓	95	↓	0.069		58		↓
(3)	0.019	0.006	6.05	0.060		75		0.047	0.0030	38	2.5	
(4)	0.019	0.011	5.90	0.040		50		0.043		36		
1975 FTP	1.62	0.11	2.19	0.020	0.015	22	16	0.004	------	3.0	---	19

TABLE E-16

EMISSIONS FROM THE PELLETED OXIDATION CATALYST SYSTEM WITH AN AGED CATALYST (AND AN AIR PUMP)

All Tests Conducted With 0.032 Wt. % Sulfur Fuel

Test Mode	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions				Sulfur Balance, Bubbler + Filter
				g/km		% of Fuel S		g/km		% of Fuel S		
	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Gokadyr-Ross, Raw Exhaust	Filter, Dilute Exhaust	Gokadyr-Ross, Raw Exhaust	
TURNPIKE DRIVING PRECONDITIONING												
1975 FTP	1.84	0.18	2.09	0.025	0.023	24	22	0.0036		2.3	---	24
20 min. idle (g/test)	0.02	0.76	1.85	0.0(a)	0.0	0	0.0	0.0003	0.014	0.04	1.7	0.04
96 km/h (1)	0.081	0.031	6.03	0.088	0.091	97	101	0.102	0.0015	75	1.1	136
↓ (2)	0.068	0.031	6.16	0.072	↓	79	↓	0.039		29		↓
↓ (3)	0.10	0.025	6.40	0.080	↓	87	↓	0.030	0.0013	22	0.9	↓
↓ (4)	0.081	0.031	6.46	0.053	↓	61	↓	0.022		16		↓
1975 FTP	1.47	0.17	2.06	0.009	0.0025	9	2.4	0.0007	------	0.4	---	2.8
CITY DRIVING PRECONDITIONING												
1975 FTP	2.93	0.22	2.49	0.030	0.032	29	29	0.0066	------	4.0	---	33
20 min. idle (g/test)	0.08	0.73	2.97	0.0(a)	0.058	0	11	0.003	0.024	0.4	3.0	11
96 km/h (1)	0.12	0.022	5.99	0.004	0.090	4.0(b)	97	0.086	0.0005	61	0.4	132
↓ (2)	0.11	0.018	5.57	0.004	↓	3.9(b)	↓	0.039		27		↓
↓ (3)	0.087	0.027	6.12	0.004	↓	4.1(b)	↓	0.038	0.0005	27	0.3	↓
↓ (4)	0.087	0.027	6.05	0.0	↓	0(a,b)	↓	0.032		24		↓
1975 FTP	1.44	0.16	2.20	0.028	0.016	29	15	0.004	------	2.6	---	18

(a) Below detection limit.
(b) Low values may have been due to air leak in TECO sampling line.

TABLE E-17

EMISSIONS FROM THE MONOLITHIC OXIDATION CATALYST SYSTEM WITH AGED Pt/Pd CATALYSTS (AND AN AIR PUMP)

All Tests Conducted With 0.032 Wt. % Sulfur Fuel

Test Mode	Gaseous Emissions, g/km			SO_2 Emissions				$SO_4^=$ Emissions				Sulfur Balance, Bubbler + Filter
				g/km		% of Fuel S		g/km		% of Fuel S		
	CO	HC	NO_x	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	TECO, Dilute Exhaust	H_2O_2 Bubbler, Dilute Exhaust	Filter, Dilute Exhaust	Goksøyr-Rose, Raw Exhaust	Filter, Dilute Exhaust	Goksøyr-Rose, Raw Exhaust	
TURNPIKE DRIVING PRECONDITIONING												
1975 FTP	2.80	0.27	1.90	0.091	0.104	81	90	0.0068	------	4.1	---	94
20 min. idle (g/test)	1.08	0.65	6.01	0.38	0.24	51	32	0.0033	0.024	0.3	2.2	32
96 km/h (1)	0.70	0.078	4.50	0.057	0.064	74	85	0.039	0.0026	34	2.2	112
↓ (2)	0.64	0.076	4.16	0.045	↓	60	↓	0.030		26		↓
(3)	0.68	0.075	4.16	0.045	↓	60	↓	0.025	0.0010	23	0.9	↓
(4)	0.70	0.077	4.01	0.049	↓	66	↓	0.028		25		↓
1975 FTP	2.73	0.22	1.94	0.088	0.117	77	97	0.0084	------	5.0	---	102
CITY DRIVING PRECONDITIONING												
1975 FTP	3.46	0.44	1.41	0.121	0.18	103	144	0.014	------	8.0	---	152
20 min. idle (g/test)	0.83	0.67	5.19	0.32	0.17	39	20	0.0009	0.025	0.1	2.0	20
96 km/h (1)	0.63	0.061	3.93	0.060	0.078	75	96	0.053	0.0063	45	5.3	125
↓ (2)	0.64	0.053	4.43	0.030	↓	36	↓	0.031	------	25	---	↓
(3)	0.55	0.053	4.57	0.025	↓	32	↓	0.028	0.0032	24	2.6	↓
(4)	0.56	0.055	4.71	0.205	↓	31	↓	0.028		22		↓
1975 FTP	2.65	0.20	1.62	0.064	0.088	53	72	0.006	------	3.4	---	75

TABLE E-18

VEHICLE DURABILITY TEST RESULTS OF PELLETED 85 CaO/10 SiO2/5% Na2O

Trap Distance (km)	Test Description	Filter, Diluted Exhaust			Trap ΔP @ 64 km/h (Pa)	$SO_4^=$ Gokadyr-Ross (gm/km)	Fuel Economy (mpg)	Hot 1975 FTP				
		Total Particulate (gm/km)	Total $SO_4^=$ (gm/km)	Total Ca (gm/km)				CO (gm/km)	HC (gm/km)	NO_x (gm/km)	Fuel Economy	
											Wt. (mpg)	Carbon Balance (mpg)
Base Car*	64 km/h	0.171	0.086	----	----	----	21.0	----	----	----	----	----
0*	64 km/h	0.012	0.002	$2.0x10^{-5}$	----	----	20.0	----	----	----	----	----
	64 km/h	0.030	0.003	$2.5x10^{-5}$	----	----	20.5	----	----	----	----	----
	1 hr. @ idle	0.023 gm	0.001 gm	$3.6x10^{-4}$ gm	----	----		----	----	----	----	----
	2 hrs.@ 97 km/h	0.007	0.001	$6.2x10^{-5}$	----	----		----	----	----	----	----
1 610*	1 hr. @ 64 km/h	0.003	0.006	----	----	----	19.5	----	----	----	----	----
1 790**	64 km/h	0.004	0.001	$1.7x10^{-4}$	----	----	18.1	----	----	----	----	----
3 220	64 km/h	0.003	0.001	$2x10^{-5}$	9 950	----	20.8	----	----	----	----	----
	64 km/h	0.004	0.001	$1x10^{-5}$	9 950	----	21.3	----	----	----	----	----
4 830	64 km/h	0.000	0.001	$2x10^{-5}$	1 320	----	20.9	----	----	----	----	----
	64 km/h	0.004	0.001	$1x10^{-5}$	1 320	----	20.4	----	----	----	----	----
6 440	64 km/h	0.003	0.004	$<3x10^{-5}$	9 700	----	20.4	----	----	----	----	----
	64 km/h	0.007	0.002	$<3x10^{-5}$	9 700	----	20.8	----	----	----	----	---

TABLE E-18 (cont.)

		Filter, Diluted Exhaust						Hot 1975 FTP				
											Fuel Economy	
Trap Distance (km)	Test Description	Total Particulate (gm/km)	Total $SO_4^=$ (gm/km)	Total Ca (gm/km)	Trap ΔP @ 64 km/h (Pa)	$SO_4^=$ Goksøyr-Ross (gm/km)	Fuel Economy (mpg)	CO (gm/km)	HC (gm/km)	NO_x (gm/km)	Wt. (mpg)	Carbon Balance (mpg)
9 650	64 km/h	0.002	0.001	----	14 900	----	14.5	----	----	----	----	----
	64 km/h	0.003	0.001	$4x10^{-5}$	22 500	----	16.5	----	----	----	----	----
12 870	64 km/h	----	0.001	$4x10^{-5}$	14 900	----	16.3	----	----	----	----	----
	64 km/h	----	0.001	$<3x10^{-5}$	22 500	----	15.7	----	----	----	----	----
17 600	64 km/h	0.013	0.001	$<3x10^{-5}$	14 900	----	16.3	----	----	----	----	----
	64 km/h	0.005	0.002	$<3x10^{-5}$	14 900	----	16.9	----	----	----	----	----
	75 FTP	0.024	0.003	$2x10^{-4}$	----	----	----	1.32	0.22	2.59	10.0	9.81
24 000	64 km/h	0.007	0.001	$3x10^{-5}$	22 500	----	14.6	----	----	----	----	----
	64 km/h	0.003	0.001	$<3x10^{-5}$	22 500	----	14.6	----	----	----	----	----
	75 FTP	0.016	0.003	$2x10^{-4}$	----	----	----	0.73	0.36	1.91	9.79	----
30 720	64 km/h	0.005	0.001	$3x10^{-5}$	22 500	----	14.5	----	----	----	----	----
	64 km/h	0.003	0.001	$<3x10^{-5}$	22 500	----	15.6	----	----	----	----	----
	75 FTP	0.014	0.001	$1x10^{-4}$	----	----	----	1.12	0.15	2.54	9.76	----
35 890	64 km/h	0.008	0.001	$<3x10^{-5}$	22 500	----	14.5	----	----	----	----	----
	64 km/h	0.004	0.001	$<3x10^{-5}$	22 500	----	14.5	----	----	----	----	----
	75 FTP	0.019	0.002	$2x10^{-4}$	----	----	----	0.80	0.33	2.00	9.49	----
42 400	64 km/h	0.008	0.005	$7x10^{-5}$	37 500-29 000	----	14.0	----	----	----	----	----
	64 km/h	0.004	0.002	$7x10^{-5}$	29 000	----	14.4	----	----	----	----	----
	75 FTP	0.017	0.002	$4x10^{-4}$	----	----	----	1.31	0.33	2.76	9.23	----

TABLE E-19

VEHICLE DURABILITY TEST RESULTS OF $CaCO_3$ CHIPS

		Filter, Diluted Exhaust						Hot 1975 FTP			Fuel Economy	
Trap Distance (km)	Test Description	Total Particulate (gm/km)	Total $SO_4^=$ (gm/km)	Total Ca (gm/km)	Trap ΔP @ 64 km/h (Pa)	$SO_4^=$ Goksøyr-Ross (gm/km)	Fuel Economy (mpg)	CO (gm/km)	HC (gm/km)	NO_x (gm/km)	Wt. (mpg)	Carbon Balance (mpg)
Base Car	64 km/h	0.044	0.026	$<3\times10^{-5}$	996	----	15.7	----	----	----	----	----
	64 km/h	0.061	0.032	$<3\times10^{-5}$	996	----	16.0	----	----	----	----	----
	'75 FTP	0.029	0.013	$<1\times10^{-4}$	----	----		1.33	0.22	1.31	9.91	9.67
	'75 FTP	0.018	0.011	$<1\times10^{-4}$	----	----		1.09	0.16	1.34	9.65	9.36
3980	64 km/h	0.034	0.017	3×10^{-5}	1992	0.019	16.1	----	----	----	----	----
	64 km/h	0.057	0.027	$<3\times10^{-5}$	995	0.020	16.6	----	----	----	----	----
	'75 FTP	0.027	0.005	1×10^{-3}	----	-----	----	1.08	0.33	1.55	10.4	10.2
11200	64 km/h	0.023	0.015	3×10^{-5}	1494	0.015	15.8	----	----	----	----	----
	64 km/h	0.036	0.020	$<3\times10^{-5}$	1494	0.023	16.3	----	----	----	----	----
	'75 FTP	0.024	0.005	1×10^{-4}	----	-----	----	1.05	0.36	1.73	10.8	11.0
17400	64 km/h	0.039	0.014	$<3\times10^{-5}$	1494	0.018	18.4	----	----	----	----	----
	64 km/h	0.057	0.022	$<3\times10^{-5}$	1494	0.022	18.5	----	----	----	----	----
	'75 FTP	0.041	0.011	2×10^{-4}	----	-----	----	0.86	0.36	2.04	10.9	11.3

TABLE E-20

VEHICLE DURABILITY TEST OF PELLETED ZINC OXIDE SORBENT

		Filter, Diluted Exhaust						Hot 1975 FTP				
											Fuel Economy	
Trap Distance (km)	Test Description	Total Particulate (gm/km)	Total $SO_4^=$ (gm/km)	Total Zinc (gm/km)	Trap ΔP @ 64 km/h (Pa)	$SO_4^=$ Goksøyr-Ross (gm/km)	Fuel Economy (mpg)	CO (gm/km)	HC (gm/km)	NO_x (gm/km)	Wt. (mpg)	Carbon Balance (mpg)
Base Case	64 km/h	0.066	0.026	$<2.8\times10^{-5}$	---	0.027	20.73	---	---	---	---	---
	64 km/h	0.090	0.035	$<2.8\times10^{-5}$	---	0.034	20.67	---	---	---	---	---
	FTP	0.080	0.036	$<1.0\times10^{-4}$	---	---	---	1.14	0.27	2.78	11.63	12.01
5 300	64 km/h	0.035	0.020	8.71×10^{-5}	750	0.029	20.29	---	---	---	---	---
	64 km/h	0.044	0.024	4.04	750	0.023	20.03	---	---	---	---	---
	FTP	0.071	0.036	30.2	---	---	---	1.54	0.29	3.07	11.58	11.75
9 700	64 km/h	0.028	0.018	4.04	500	0.033	19.73	---	---	---	---	---
	64 km/h	0.039	0.023	<2.80	500	0.034	20.00	---	---	---	---	---
	FTP	0.049	0.036	20.2	---	---	---	0.83	0.13	2.50	11.74	12.12
15 900	64 km/h	0.029	0.017	3.1	500	0.044	21.56	---	---	---	---	---
	64 km/h	0.042	0.022	<2.8	500	0.046	22.02	---	---	---	---	---
	FTP	0.076	0.042	17.9	---	---	---	0.60	0.13	3.87	12.48	12.77

TABLE E-21

VEHICLE DURABILITY TEST RESULTS OF RINGED 85 CaO/10 SiO_2/5% Na_2O

		Filter, Diluted Exhaust						Hot 1975 FTP				
											Fuel Economy	
Trap Distance (km)	Test Description	Total Particulate (gm/km)	Total $SO_4^=$ (gm/km)	Total Ca (gm/km)	Trap ΔP @ 64 km/h (Pa)	$SO_4^=$ Goksøyr-Ross (gm/km)	Fuel Economy (mpg)	CO (gm/km)	HC (gm/km)	NO_x (gm/km)	Wt. (mpg)	Carbon Balance (mpg)
Base Case	64 km/h	0.065	0.033	$<3\text{x}10^{-5}$	500	0.028	21.3	----	----	----	----	----
	64 km/h	0.084	0.032	$<3\text{x}10^{-5}$	500	0.035	22.1	----	----	----	----	----
	75 FTP	0.038	0.025	$<1\text{x}10^{-4}$	----	----	----	0.62	0.07	2.96	11.7	11.6
3 028	64 km/h	0.008	0.004	Not	622	0.029	21.5	----	----	----	----	----
	64 km/h	0.009	0.005	Submitted	622	0.031	21.5	----	----	----	----	----
	75 FTP	0.020	0.011	"	----	----	----	3.18	0.24	2.86	11.5	11.4
4 105	64 km/h	0.007	0.004	$<3\text{x}10^{-5}$	500	0.031	22.1	----	----	----	----	----
	64 km/h	0.008	0.006	$<3\text{x}10^{-5}$	500	0.022	22.8	----	----	----	----	----
	75 FTP	0.013	0.006	$1\text{x}10^{-4}$	----	----	----	2.17	0.08	3.09	11.6	11.4
7 662	64 km/h	0.008	0.004	$<3\text{x}10^{-5}$	1 000	0.034	22.2	----	----	----	----	----
	64 km/h	0.011	0.006	$<3\text{x}10^{-5}$	1 000	0.022	22.2	----	----	----	----	----
	75 FTP	0.012	0.005	$<1\text{x}10^{-4}$	----	----	----	1.99	0.09	3.83	11.7	11.7
11 024	64 km/h	0.019	0.009	$<3\text{x}10^{-5}$	3 000	0.018	21.8	----	----	----	----	----
	64 km/h	0.024	0.014	$<3\text{x}10^{-5}$	3 000	0.024	21.8	----	----	----	----	----
	75 FTP	0.018	0.004	$1.1\text{x}10^{-4}$	----	----	----	2.30	0.26	3.42	11.4	11.2
14 400	64 km/h	0.033	0.016	$<3\text{x}10^{-5}$	3 700	0.025	21.7	----	----	----	----	----
	64 km/h	0.038	0.022	$<3\text{x}10^{-5}$	3 700	0.025	21.5	----	----	----	----	----
	75 FTP	0.017	0.006	$<1\text{x}10^{-4}$	----	----	----	7.82	0.29	3.36	11.5	10.9
20 400	64 km/h	0.019	0.009	$3\text{x}10^{-5}$	4 200	0.010	21.3	----	----	----	----	----
	64 km/h	0.026	0.013	$3\text{x}10^{-5}$	4 200	0.017	21.5	----	----	----	----	----
	75 FTP	0.021	0.008	$2.6\text{x}10^{-4}$	----	----	----	4.83	0.75	3.33	11.4	11.0

TABLE E-22

LABORATORY SCREENING OF SORBENT MATERIALS

Sorbent Volume = 13 cm^3 Temperature = 480°C (370°C where indicated) Space Velocity = 100 000 v/v/h

Feed Gas Composition: CO_2 = 12%; H_2O = 12%; SO_2 = 15 ppm; H_2SO_4 = ~4 ppm; NO_x = 500 ppm; O_2 = 3%; balance N_2

Sorbent	Shape	Weight, grams	Time On Feed, Hrs.	H_2SO_4 Out, ppm	Sulfate Trapping Efficiency, %	SO_2 Out, ppm	SO_2 Trapping Efficiency, %	Relative Ease of Pilling
85 CaO/10 SiO_2/5 Na_2O (Benchmark)	pellets 3.2 mm	11.0	1	0	100	1	93	good
Al_2O_3 (Norton 4102)	pellets 3.2 mm	14.5	1.3 2.6	1.9	55	14	7	----
BaO**	granules ~3 mm	38.1	---	---	---	---	---	----
80 CaO/20 SiO_2	pellets 3.2 mm	11.3	2.5	0	100	13	15	fair
ZrO_2 (Harshaw)	pellets 3.2 mm	24.7	1.3 4.0 5.1* 8.8*	0 0.6 0.9 2.9	100 84 73 12	15 15 15 15	0 0 0 0	----
Benchmark	pellets 3.2 mm	12.7	2.3	0.1	97	1	93	good
Ca SiO_3 (Micro-Cel)	pellets 3.2 mm	5.7	1.3 3.5	0 0.1	100 97	13 14	15 7	poor
MgO (Calcined $Mg(OH)_2$)	pellets 3.2 mm	20.2	1.3 4.5	0 0	100 100	15 15	0 0	poor
MgO (Calcined Magnesite)	spheres 3-5 mm	11.7	1.3 2.7 4.0* 7.4	0 0.3 0 0	100 92 100 100	15 15 15 ---	0 0 0 ---	----
MgO (Harshaw)	pellets 3.2 mm	16.8	1.3 2.7 4.2	0 1.0 3.2	100 74 17	15 15 15	0 0 0	----

TABLE E-22(CONT.)

Sorbent	Shape	Weight, grams	Time On Feed, Hrs.	H_2SO_4 Out, ppm	Sulfate Trapping Efficiency, %	SO_2 Out, ppm	SO_2 Trapping Efficiency, %	Relative Ease of Pilling
85 MgO/10 SiO_2/5 Na_2O	granules 6/10 mesh	5.7	2.2	0	130	7.9	47	unsuccessful
$CaCO_3$ (Marble)	chips 7/10 mesh	20	1.3	1.0	74	15	0	unsuccessful
			3.7	1.9	50	15	0	
ZnO (Harshaw)	extrudate 5 mm	17.7	1.2	0	100	14	7	----
			3.9	0.7	82	---	---	
			4.5*	0	100	15	0	
			8.2*	1.4	58	15	0	
Benchmark	pellets 3.2 mm	13.3	3.9*	0	100	3.1	79	good
			8.4*	0	100	9.7	35	
CaO (3% aluminum stearate binder)	pellets 3.2 mm	10.6	1.0*	0	100	10	33	fair
			3.2*	0	100	---	---	
			4.6*	1.1	67	13.2	12	
Al_2O_3 (MCB activated)	pellets 3.2 mm	13.1	1.2	0.2	94	15	0	----
			3.6	2.6	21	15	0	
			4.9	3.4	0	15	0	
MnO_2	granules 10/16 mesh	26.9	1.2	0	100	6.7	55	----
			2.7	0	100	11.9	21	
			3.9	0.6	82	11.9	21	
Al_2O_3 (washcoat, Corning)	coated honeycomb	6.4	1.3	2.0	64	15	0	----
			4.1	4.1	25	---	---	
			4.4	4.7	14	---	---	

* 370°C

** Rapidly hydrated to $Ba(OH)_2$ and dissolved

TABLE E-23

LABORATORY SCREENING OF SORBENT MATERIALS EFFECT OF SPACE VELOCITY

Sorbent Volume = 13 cm^3 Temperature = 480°C (370°C where indicated)   Feed Gas Composition = See Table E-22

Sorbent	Shape	Weight, grams	Time On Feed, Hrs.	H_2SO_4 Out, ppm	Sulfate Trapping Efficiency, %	SO_2 Out, ppm	SO_2 Trapping Efficiency, %	Space Velocity, v/v/hr.
Benchmark	pellets 3.2 mm	13.5	9.6	0.6	82	---	---	150 000
			12.6	0	100	---	---	
			14.5	0	100	12	20	
MgO (Calcined Magnesite)	spheres 3-5 mm	11.9	8.7	0.7	79	13.7	9	150 000
			11.6	2.0	40	14.3	5	
ZnO (Harshaw)	Extrudate 5 mm	17.7	9.3	1.9	50	15	0	150 000
			11.8	0	100	---	---	
Benchmark	pellets 3.2 mm	7.9	1.2	0	100	3.3-4.4	78-71	150 000
			3.2	0	100	6.3	58	
			4.2	0.1	97	7.2	52	
Benchmark*	pellets 3.2 mm	8.2	1.2	0	100	---		150 000
			2.8	0	100	4.2	72	
			4.7	3.5	36	7.0	53	
MgO* (Calcined Magnesite)	spheres 3-5 mm	11.4	1.2	0.2	96	15	0	150 000
			3.1	1.2	78	15	0	
			5.0	2.4	56	15	0	
MnO_2*	granules 10/16 mesh	25.5	1.2	0	100	14	7	150 000
			3.8	2.2	60	---	---	
			6.7	4.9	11	---	---	
Benchmark	pellets 3.2 mm	7.9	10.6	0	100	6.6	60	50 000
			12.6	0	100	7.1	57	
			14.1	0	100	7.0	58	